2-12-2015

Natural Dissipation of MTBE in Groundwater at UST Sites Following the Connecticut Ban in 2004

Graham J. Stevens
University of Connecticut - Storrs, graham.stevens@uconn.edu

Natural Dissipation of MTBE in Groundwater at UST Sites Following the Connecticut Ban in 2004

Graham Joseph Stevens

B.A., Clark University, 1998

A Thesis

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Masters of Science

At the

University of Connecticut

2015

APPROVAL PAGE

Masters of Science Thesis

Natural Dissipation of MTBE in Groundwater at UST Sites Following the Connecticut Ban in 2004

Presented by

Graham Joseph Stevens, B.A.

Major
Advisor _____
Gary A. Robbins

Associate
Advisor _____
Lanbo Liu

Associate
Advisor _____
Glenn Warner

University of Connecticut

2015

Acknowledgments

The funding for this research was provided by a grant from Weston Solutions, Inc. and I would like to thank Bette Nowak from Weston Solutions, Inc. for her support.

This work and my studies in the field of Water Resources would not have occurred if not for Dr. Gary Robbins and for his inspiration and guidance, in matters of academia and life, I thank him.

The members of my advisory committee, Dr. Lanbo Liu and Dr. Glenn Warner, also deserve thanks for their assistance with my thesis, their patience in its offering, and their guidance in the earlier years of my academic pursuit.

A sincere thank you also goes to Meredith Metcalf who assisted with the data collection and this research. Without her help, I would have been alone in my review of countless environmental reports.

Lastly, and certainly not least, thank you to Camille Fontanella for her encouragement and technical editing abilities.

Table of Contents

APPENDIX D - Semi-Log Trend Plots of MTBE Concentration

List of Figures

List of Tables

Abstract

This study was conducted to evaluate trends in MTBE contamination in groundwater and the rate of dissipation of contamination at gasoline stations in Connecticut following the January 2004 Ban of MTBE in gasoline. Statistical evaluations were conducted using pre- and post-ban data for 22 gasoline stations (83 monitoring wells), representing a range of geologic, hydrogeologic and anthropogenic conditions in Connecticut. The Wilcoxon Signed-Rank test for comparison of mean pre-ban and post-ban MTBE concentration for each site supported a decrease in concentration after the ban at 18 of the 22 sites. Dissipation of MTBE was further supported with the analysis of individual monitoring wells, which showed a decrease in MTBE in 68 of the 83 monitoring wells. Using data from the first two years after the ban from wells exhibiting a decrease in MTBE since the ban (68), the MTBE dissipation was modeled as a first order rate process. An average dissipation half-life of 7.3 months was calculated. The first order models developed using data from the first two years after the ban reasonably predicted observed conditions four years after the ban.

Chapter 1. Introduction

Beginning in 2000, there was a strong public outcry over the use of methyl *tert*-butyl ether (MTBE) as an additive to gasoline in certain states and counties in the country. The federal mandate to boost oxygen content and approval of the petroleum industry's use of MTBE to meet this mandate, imposed by the United States Environmental Protection Agency (EPA), was seen by many as a decision to protect the environment without a complete understanding of the systems that could be impacted. Air quality was improved in certain areas of the country due to the use of MTBE, but those areas have also seen widespread groundwater degradation as a result of this additive. When released to the groundwater, MTBE has proven far more difficult to remediate than other components of gasoline, posing a high risk to groundwater quality, and thereby, drinking water sources.

Public opinion and concern over the use of MTBE was greatest in the areas where MTBE was added to gasoline to boost oxygen levels, given that these were the areas with the highest incident of MTBE groundwater pollution (Grady, 2003). Public criticism of the decision to add MTBE to gasoline to meet the oxygenate mandate resulted in many states requesting a waiver from the oxygenate requirement under the Clean Air Act (NEIWPCC and NESCAUM 2001). In addition, many states acted through legislative decree to completely ban MTBE or partially ban MTBE (only allowing trace concentrations of MTBE in gasoline at less than 1 percent MTBE by volume). Iowa, Minnesota, and Nebraska instituted partial bans of MTBE in July 2000 and were eventually followed by sixteen other states.

Complete bans began with Colorado in April 2002, Michigan and California in 2003, Connecticut and New York in January 2004, and Vermont in January 2007 (EPA, 2007). These partial or complete bans constitute action to eliminate the use of MTBE in twenty-five states, whereas its use was only ever mandated through the Clean Air Act in eighteen states.

Support for elimination or substitution of MTBE was strong in the Northeastern states, especially where groundwater is a major source of drinking water. Beginning in 2004, Connecticut and New York instituted bans on the sale of gasoline with MTBE (CT DEP, 2004), and other Northeastern states have followed suit. Maine opted out of their voluntary involvement in the RFG program in March 1999 (Clavet 2004) and also voted to prohibit MTBE in gasoline, effective January 2007. Massachusetts, Rhode Island, New Hampshire, New Jersey, and Vermont also have passed legislation banning the sale of MTBE-containing gasoline (EPA, 2007). These legislative actions by the states eventually resulted in federal action through the Energy Policy Act of 2005 that effectively eliminated the use of MTBE through changes to the oxygenate requirements for gasoline (PL 109-58).

Studying the effect of a ban on MTBE in Connecticut has value for other states that have banned MTBE, as these states can use this evaluation for planning purposes, as impacted aquifers are evaluated for remediation. In addition, an evaluation of the effects of a ban on MTBE can assist policy-makers in determining what to expect with groundwater quality improvements over time. Although it has

been several years since Connecticut stopped selling MTBE-containing gasoline, the effects of this ban have not been thoroughly investigated. It is known that MTBE continued to be prevalent in groundwater after the ban, but it is not known if this contamination is attenuating and if so, at what rate. Leahy (2006) has evaluated the effect of this ban on the quality of groundwater used for public drinking water wells. However, the effect of the ban on areas where MTBE was the most likely to have been released in the greatest quantity and concentration – retail gasoline stations – has not yet been investigated.

This study was undertaken to determine the degree of decrease in MTBE groundwater contamination at or near retail gasoline station source areas following the Connecticut ban and to test the use of first order rate models as a means to estimate future groundwater concentrations.

Study Objectives

The main objectives of this study are:

- To determine if MTBE dissipates at gasoline stations after the ban on MTBE from gasoline;
- To evaluate if there is a difference in the pre-ban and post-ban data sets, and if so, how do they differ;
- To determine if MTBE dissipation follows a zero order or first order decay model;
- To evaluate characteristics that may influence the dissipation value of MTBE; and
- To calculate an average dissipation half-life value for MTBE.

Chapter 2. Background

The use of gasoline-powered motor vehicles affects air and groundwater quality, posing risks to human health and the environment. Gasoline combustion impacts air quality with the release of carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxide species (NO_x), and volatile organic compounds (VOCs), including MTBE. CO_2, CO, and NO_x are all classified as greenhouse gases, trapping heat in the atmosphere. Their effects on global climate have been the central reasons to improve fuel efficiency, to decrease vehicle miles traveled, and to promote the use of alternative fuels. Ground-level ozone formation from the reaction of NO_x and VOCs in the atmosphere is also a major concern, particularly in urban areas during summer months, as this oxidant can cause respiratory distress (Gaffney and Marley, 2009). In addition, VOCs, specifically the human carcinogen benzene and the potential human carcinogen MTBE, pose a risk of toxicity (EPA, 1997).

The ubiquitous nature of gasoline – present in mobile sources, such as cars, boats and lawnmowers, and in stationary point sources, such as service stations, refineries and bulk storage facilities – creates a risk to groundwater quality if spilled or otherwise released. In addition, because gasoline is stored in underground storage tanks (USTs) at gasoline stations to reduce fire hazards, releases to the subsurface often go unnoticed. Unfortunately, USTs have a high probability of release, due to their construction, lack of maintenance, and high probability of spillage during filling. This is evident based on data collected by EPA from 1988 to 2008, during which time EPA received 479,817 reports of releases from USTs

across the nation out of the 623,319 active and 1,695,558 closed registered USTs (EPA, 2008a). This indicates that twenty-one (21) percent of these USTs were subject to a release. While newer USTs with cathodic protection, overfill sumps, strike plates, spill buckets, and release detection have decreased the probability of UST releases, these newer systems are not spill-proof.

Young and Couch estimated the probability of a release from an active UST system by performing regression analysis on data from EPA's Corrective Action Database. The result of their analysis was a release probability of 2.6 percent of USTs per year during a six-year study period (Young and Couch, 1998). Using this release probability, 253 of the 9,737 active USTs in Connecticut would experience one release per year. Releases of gasoline from a UST system will create a groundwater contaminant plume proportional in size to the release, local hydrogeologic conditions and also the chemical properties of the pollutant, such as its solubility in water. Dissolved gasoline constituents, such as benzene, toluene, ethylbenzene, xylenes, and oxygenates, in groundwater can pose a risk to those who rely on groundwater as a source of drinking water.

Releases to the environment need not be catastrophic to cause widespread groundwater pollution. Squillace *et al*. reported that one gallon of MTBE-containing reformulated gasoline (RFG) in four million gallons of water would result in a concentration of twenty (20) µg/L MTBE (1997). In an unconsolidated aquifer with a porosity of 0.3, this plume would have a volume of approximately

36.5 acre-feet, indicating that this relatively small release could result in extensive contamination. Most releases of gasoline far exceed one gallon over the duration of the release, and releases can be frequent. EPA has estimated that approximately nine million gallons of gasoline are released to the environment each year (2008c).

In part to address the ozone issue that was becoming problematic in the late 1970s and 1980s in large urban areas, Congress passed amendments to the Clean Air Act in 1990. These amendments required the use of RFG in certain areas of the country that were subjected to unacceptable levels of ozone pollution. Section 211(k) of the Clean Air Act went into effect on January 1, 1995 and required the use of RFG in certain areas to reduce the emissions that result in ozone formation and to reduce the amount of air toxins. RFG was required to be two percent oxygen by weight and, therefore, needed to contain oxygenated compounds or oxygenates, the most prevalent of which in the 1990s and 2000s was MTBE. Since lead began to be phased-out of on-road vehicles in 1973, a replacement octane booster was needed. In 1979, MTBE began to be used in low levels to boost the octane of gasoline in the United States. During the height of MTBE use in the 1990s and early 2000s, conventional gasoline contained approximately three percent to eight percent MTBE (depending on the gasoline blend) for its octane boosting properties; whereas, RFG contained at least eleven (11) percent MTBE to meet the two percent oxygen by weight requirement (EPA, 2008b).

RFG was originally mandated by EPA in the 1990 Amendments to the Clean Air Act to be utilized in nine metropolitan areas where ozone levels were most problematic. These mandated areas were Los Angeles, San Diego, Chicago, Houston, Milwaukee, Baltimore, Philadelphia, Hartford, and New York City. Additional areas with air quality issues related to mobile sources were permitted to "opt-in" to the program (Energy Information Administration, 1999). RFG that utilized MTBE to boost oxygen levels was first used in California in the late 1980s. The program's success and the industry's desire to quickly implement a RFG program resulted in modifications to the proposed amendments to the Clean Air Act (EPA, 1995). Between the nine mandated areas and over twenty-five (25) additional opt-in areas, approximately thirty-five (35) percent of the population of the United States utilized RFG by 1997 (Energy Information Administration, 1999). This corresponded to approximately 39.7 million liters of MTBE used every day in the United States (Delzer and Ivahnenko, 2003). The RFG program is widely considered successful at improving air quality through reduction of ozone and air toxins. However, it is now known that MTBE became a common contaminant of drinking water sources, particularly in areas of higher MTBE use.

Around the same time that the amount of MTBE added to gasoline increased under the RFG program, there was a growing frequency of MTBE detections in public and private water supplies. In 1999 and 2000, the U.S. Geological Survey (USGS) conducted a random sampling of drinking water sources in the United States. The national survey documented that MTBE was present at some detectable level in

8.7 percent of the samples collected. Further, the USGS noted that the detections of MTBE increased fivefold to nearly a quarter of all drinking water sources in areas that were in the RFG program (Grady, 2003). USGS had previously found in a targeted study of the Northeastern and Mid-Atlantic States that MTBE was detected in nine percent of the community water systems, and MTBE was detected in twenty (20) percent of wells sampled with RFG use areas (Zodorski *et al*., 2001).

These detections in drinking water should have been anticipated, given the characteristics and use of MTBE. MTBE has a very high solubility in water at 51,000 milligrams per liter (mg/L) at 25 °C (EPA, 2008c). In comparison, benzene has a solubility of only 1,780 mg/L. In its pure form, MTBE is almost thirty (30) times more soluble in water. When MTBE is a component of RFG, it can partition into water at a concentration of about 4,700 mg/L (at 20 °C). This concentration is 261 times higher than that expected for benzene. (Kinner, 2001). The high solubility of MTBE makes it highly prone to dissolving into infiltrating precipitation that moves into the subsurface through RFG-contaminated soil.

During saturated flow, aqueous organic constituents flow with groundwater but their relative velocity is retarded proportionally to their affinity to organic matter. The organic carbon coefficient (K_{oc}) is used to describe the magnitude of a compound's affinity to organic matter. MTBE has a $\text{Log } K_{oc}$ of 0.55 to 0.91 (Fayolle *et al*., 2001). Since other gasoline constituents have a higher affinity to organic matter in soil, with benzene having a K_{oc} approximately an order of magnitude

greater than that of MTBE, MTBE is more likely to impact groundwater (EPA, 2008c). MTBE transport in groundwater will likely be at a rate similar to the movement of water itself (Rice *et al*., 1995 and Squillace *et al*., 1998).

Groundwater impacts are probable from other release mechanisms as well. With the Henry's law constant for MTBE calculated to be 0.0216 at 25 °C (Robbins *et al*., 1993), MTBE is not as volatile as other components of gasoline, such as BTEX (benzene, toluene, ethylbenzene, and xylenes). Robbins and others (1993) calculated the Henry's law constants for benzene, toluene, ethylbenzene, and o-xylene at 25 °C to be 0.216, 0.263, 0.318, and 0.204, respectively. MTBE, therefore, is approximately an order of magnitude less volatile than the BTEX compounds. USGS classifies compounds with a Henry's law constant greater than 0.05 as very volatile (Squillace *et al*., 1998). While MTBE is volatile, its lower volatility would result in greater volatilization of BTEX compounds from a spill of gasoline, leaving MTBE preferentially available to infiltrate to groundwater. Based on its high affinity for water, MTBE that does volatilize into the atmosphere may return to the ground surface dissolved in precipitation (Squillace *et al*., 1997). This precipitation can infiltrate the ground and recharge groundwater, thereby creating another pathway for MTBE to groundwater.

Regardless of the release mechanism, once pore water containing MTBE has reached the phreatic surface, movement of MTBE will be controlled by the factors that control groundwater flow, such as hydraulic conductivity, gradient, and

dispersion (Freeze and Cherry, 1979). Transport of aqueous organics in groundwater will be retarded by sorption to aquifer materials. However, MTBE shows little affinity for partitioning to the organic fraction of aquifer materials and suspended solids (Fayolle *et al*., 2001). A compound's affinity for sorption can be represented by its Retardation Factor (Rf), which is the ratio of the velocity of groundwater to the velocity of the compound. The Rf value for MTBE is close to one under typical conditions and will move at a velocity near that of groundwater (Zodorgski *et al*., 1997 and Keller *et al*., 1998b). In fact, Robbins and Gilbert (2000) have suggested that MTBE can be used as a conservative tracer for estimating contaminant transport processes because it travels at a similar velocity to the groundwater and faster than other dissolved gasoline compounds in a contaminant plume.

The extent to which MTBE can be considered a conservative tracer is dependent on the degree of site-specific intrinsic bioremediation. In order for MTBE to be appreciably affected by degradation, indigenous microbes must be able to readily transform MTBE. Biodegradation has been shown to occur under aerobic or anaerobic conditions, with rates under anaerobic conditions generally slower, but rates of biodegradation vary widely based on the site of study (Davis and Erickson, 2004 and Finneran and Lovely, 2001). Davis and Erickson (2004) note that field studies have seen dissipation half-lives for MTBE as low as 1.7 days under aerobic conditions and sixty-nine (69) days under anaerobic conditions, with most calculated values much longer. Yeh and Novak (1994) demonstrated that MTBE

was degraded in anaerobic conditions, but only when the soil had a low organic content and pH was near 5.5. Obviously, these conditions are not present at all sites, and microbes may show preference for other organics present in groundwater contaminated with MTBE. Keller and others (1998b) suggested that the relatively recent introduction of MTBE into the environment has not provided sufficient time for indigenous microbes to develop adequate systems to degrade MTBE. It has also been suggested that these microbes will develop, but the speed of their development will likely not be sufficient to limit the migration of MTBE plumes that travel at the same velocity as groundwater (Finneran and Lovely, 2001). These factors all contribute to MTBE plumes extending further and with greater velocities than BTEX from the same release (Landmeyer et al. 1998) and have contributed to the ubiquitous nature of MTBE groundwater contamination.

Chapter 3. Methods

Site Selection

In order for the results of this study to be representative of the various geologic, hydrogeologic, and UST site conditions, sites were selected from a list of all retail gasoline stations in Connecticut that conducted long-term groundwater monitoring. Files on record at the Connecticut Department of Energy and Environmental Protection (CTDEEP) were exhaustively reviewed to find sites that meet the following criteria during the four-year study period (two years before and two years after the January 2004 ban):

- Site used as a retail gasoline station;
- At least one active, registered underground storage tank (UST) on site;
- MTBE contamination observed in source area or near-field, downgradient monitoring wells prior to ban;
- Sufficient quantity and consistency in frequency of groundwater monitoring events;
- No free product observed or apparent at the site; and
- Site not undergoing active remediation (e.g., soil-venting system, groundwater pump-and-treat system, source area excavation).

These six selection criteria were necessary to put specific constraints on the data utilized for this study. Sites selected must have been consistently used as a retail gasoline station with at least one active UST to ensure that each site has approximately the same risk of release of gasoline during the study period.

Further, confirmed releases prior to the study period are necessary at each site in order for MTBE groundwater concentration trends to be evaluated. Although a confirmed release is necessary, these sites should not have continuing, on-going sources of contamination, such as the presence of free-phase product on the groundwater table or soil that has free-draining petroleum. Additionally, the quantity of monitoring events used to evaluate any such trends must not be a limiting factor on the significance of any statistical evaluation. These sites will likely have residual contamination, but the process of eliminating sites with observed or apparent free product will remove from the data set sites where MTBE concentrations will likely not attenuate at a rate associated with natural processes; that is, the free-phase product would be the primary controlling factor in the concentration of MTBE in groundwater. Finally, active remediation would artificially influence many of the natural processes that control the migration and dissipation of MTBE; therefore, sites with active remediation must not be included.

CTDEEP files from the Remediation Division, Leaking Underground Storage Tank Program, and Underground Storage Tank Petroleum Clean Up Account Program were reviewed to find sites that meet these criteria. Hundreds of potential sites were reviewed for inclusion in the study, but a majority of the sites were excluded due to a conflict with one or more of the selection criteria. Twenty-two (22) retail gasoline stations were ultimately selected for this study.

The selected sites were located in multiple towns in Connecticut and represent a range of geologic, hydrogeologic, and anthropogenic conditions. The approximate location of each site is shown on **Figure 3-1**.

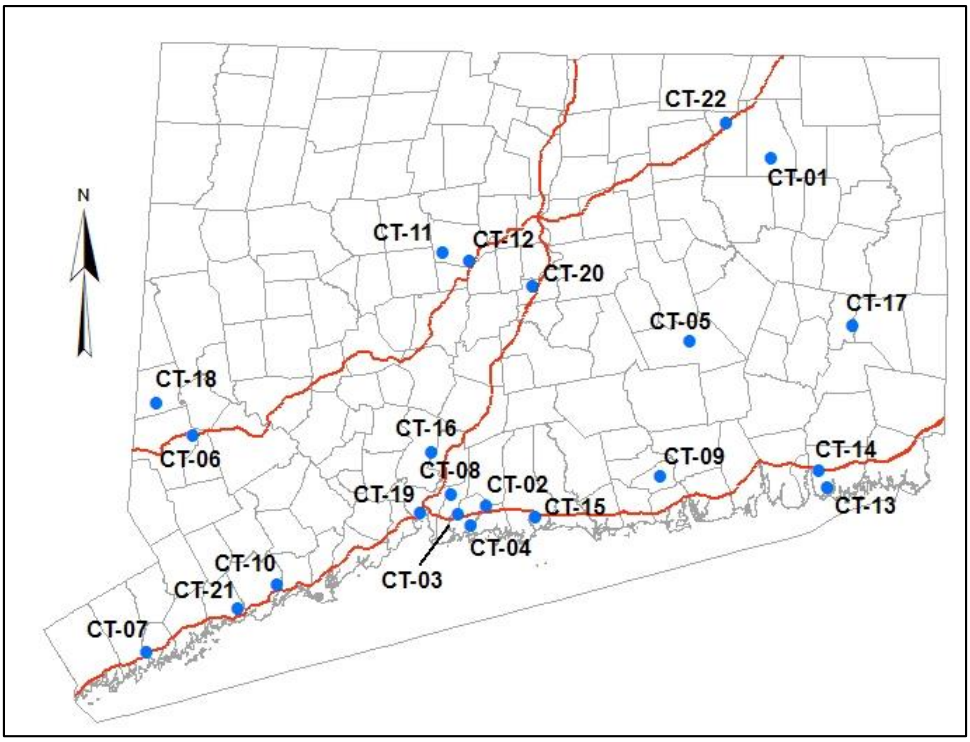


Figure 3-1 Approximate location of retail gasoline station sites used in this study.

Certain selection criteria were also used to determine which monitoring wells from each site were appropriate for use in the study. Monitoring wells located adjacent to or in close proximity to known or potential source areas (USTs or dispensing pumps) that could be shown to be hydraulically downgradient of the known or potential source areas were considered. Groundwater quality in close proximity to the known or potential source areas is more likely to have higher concentrations of MTBE from recent releases than groundwater at greater distances. Further,

natural processes will decrease MTBE concentrations in groundwater as it travels away from a source. Since groundwater plumes are subject to minor temporal variations in the lateral direction, data from the center of a groundwater plume is less affected by these changes that would result in increases or decreases in concentrations over time that are not the result of dissipation but are merely the result of shifting of the plume flow direction. Monitoring wells that are hydraulically downgradient of known or potential source areas would likely represent groundwater quality in the center of the groundwater plume. In limited instances, sites were rejected when groundwater head elevation data were not available to determine groundwater flow direction.

Monitoring wells were further excluded from consideration based on the number of monitoring events with available data over the study period. Initially, this study intended to use only monitoring wells that had consistent, quarterly groundwater monitoring events throughout the study period. However, it became apparent that this frequency of data collection was not common practice. As a result of this discovery, data from monitoring wells were reviewed to ensure a sufficient number of samples from before and after the ban were available. Preference was given to sites with a greater number of sampling rounds during the study period, to limit the impact of smaller sample sizes on the data evaluation. Monitoring data were further screened to include wells with an elevated concentration of MTBE in pre-ban monitoring results. Preference was given to monitoring wells that had initial concentrations of MTBE greater than 100 micrograms per liter (µg/L). Higher

starting concentrations of MTBE were preferentially selected to ensure concentrations persisted for the duration of the study period.

Once sites were selected, various site characteristics were noted for use in evaluating the results of this study. The typical information available in documents submitted to the CTDEEP related to the surficial materials of the site and surrounding area, the type of formation monitored, and locations of monitoring wells relative to other site features. Surficial materials, for the purposes of this study, were categorized as sand and gravel or till, fill and other deposits. Sand and gravel represents more permeable of the two surficial material classifications. **Table 3-1** lists each site by Site ID and Town and presents the surficial material information and number of wells used from each site. **Figure 3-2** depicts the breakdown of sites per surficial materials category.

Data available on the type of formation being sampled by each monitoring well was limited to overburden or bedrock. **Table 3-1** also identifies the formation screened by the well and whether each monitoring well is a source area or near field monitoring well. For the purposes of this study, any well greater than fifty (50) feet from the USTs or dispensing pumps was categorized as a near field monitoring well. Wells closer than fifty (50) feet were categorized as source area monitoring wells.

Table 3-1. Site and Monitoring Well Characteristics.

Site ID	Site Name	Surficial Materials	Wells	Distance	Screened Unit
CT-01	Ashford	Sand and Gravel	MW-1	Source Area	Overburden
			MW-2	Source Area	Overburden
			MW-3	Near Field	Overburden
			MW-4	Near Field	Overburden
CT-02	Branford-1	Till, Fill or Other Deposits	MW-1	Near Field	Overburden
			MW-2	Near Field	Overburden
			MW-3	Near Field	Overburden
			MW-4	Source Area	Overburden
CT-03	Branford-2	Till, Fill or Other Deposits	MW-1	Source Area	Overburden
			MW-2	Source Area	Overburden
			MW-3	Source Area	Overburden
			MW-4	Source Area	Overburden
			MW-5	Near Field	Overburden
CT-04	Branford-3	Till, Fill or Other Deposits	MW-1	Source Area	Overburden
			MW-2	Near Field	Overburden
			MW-3	Near Field	Overburden
			MW-4	Near Field	Overburden
CT-05	Colchester	Sand and Gravel	MW-1	Near Field	Bedrock
			MW-2	Near Field	Bedrock
			MW-3	Near Field	Bedrock
			MW-4	Near Field	Bedrock
CT-06	Danbury	Till, Fill or Other Deposits	MW-1	Near Field	Bedrock
			MW-2	Near Field	Bedrock
CT-07	Darien	Till, Fill or Other Deposits	MW-1	Near Field	Overburden
			MW-2	Source Area	Overburden
			MW-3	Near Field	Overburden
			MW-4	Near Field	Bedrock
CT-08	East Haven	Till, Fill or Other Deposits	MW-1	Source Area	Overburden
			MW-2	Source Area	Overburden
			MW-3	Source Area	Overburden
			MW-4	Source Area	Overburden
CT-09	Essex	Sand and Gravel	MW-1	Source Area	Overburden
			MW-2	Source Area	Overburden
			MW-3	Source Area	Overburden
CT-10	Fairfield	Till, Fill or Other Deposits	MW-1	Source Area	Overburden
			MW-2	Source Area	Overburden
			MW-3	Source Area	Overburden
			MW-4	Source Area	Overburden
CT-11	Farmington-1	Sand and Gravel	MW-1	Near Field	Overburden
			MW-2	Near Field	Overburden

CT-12	Farmington-2	Sand and Gravel	MW-1	Source Area	Overburden
			MW-2	Source Area	Overburden
			MW-3	Near Field	Overburden
			MW-4	Near Field	Overburden
			MW-5	Near Field	Overburden
			MW-6	Near Field	Overburden
			MW-7	Source Area	Overburden
CT-13	Groton	Sand and Gravel	MW-1	Source Area	Overburden
			MW-2	Source Area	Overburden
			MW-3	Source Area	Overburden
			MW-4	Source Area	Overburden
			MW-5	Source Area	Overburden
CT-14	Groton	Till, Fill or Other Deposits	MW-1	Near Field	Overburden
			MW-2	Source Area	Overburden
CT-15	Guilford	Sand and Gravel	MW-1	Source Area	Overburden
			MW-2	Source Area	Overburden
			MW-3	Source Area	Overburden
CT-16	Hamden	Sand and Gravel	MW-1	Source Area	Overburden
			MW-2	Source Area	Overburden
CT-17	Lisbon	Sand and Gravel	MW-1	Source Area	Overburden
			MW-2	Source Area	Overburden
CT-18	New Fairfield	Till, Fill or Other Deposits	MW-1	Near Field	Overburden
			MW-2	Source Area	Overburden
			MW-3	Source Area	Overburden
CT-19	New Haven	Till, Fill or Other Deposits	MW-1	Near Field	Overburden
			MW-2	Near Field	Overburden
			MW-3	Near Field	Overburden
			MW-4	Near Field	Overburden
CT-20	Rocky Hill	Till, Fill or Other Deposits	MW-1	Source Area	Overburden
			MW-2	Source Area	Overburden
			MW-3	Source Area	Overburden
CT-21	Westport	Till, Fill or Other Deposits	MW-1	Source Area	Overburden
			MW-2	Source Area	Bedrock
			MW-3	Near Field	Bedrock
			MW-4	Source Area	Bedrock
			MW-5	Near Field	Bedrock
			MW-6	Near Field	Bedrock
			MW-7	Near Field	Bedrock
			MW-8	Near Field	Bedrock
			MW-9	Near Field	Bedrock
CT-22	Willington	Sand and Gravel	MW-1	Source Area	Overburden
			MW-2	Source Area	Overburden
			MW-3	Source Area	Overburden

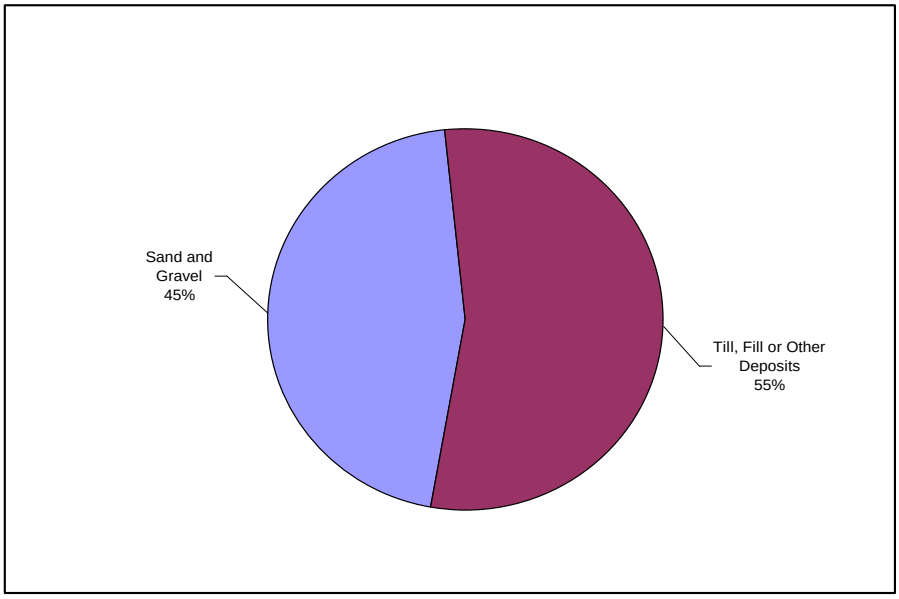


Figure 3-2 Percentage of sites in surficial material categories.

Data Evaluation

A total of eighty-three (83) monitoring wells from the twenty-two (22) selected sites were chosen for use in this study. A minimum of two monitoring wells and a maximum of nine monitoring wells were selected from each site. In addition to the data in **Table 3-1**, the following data were also collected for each monitoring well used in the study and can be found in **Appendix A**:

- Date sampled;
- MTBE concentration;
- Total BTEX concentration, if available; and
- Groundwater head elevation.

This data and the data in **Table 3-1** from each site and for each monitoring well were entered into Microsoft ® Excel ® (version 2007). **Appendix A** contains data tables for each site. Also in **Appendix A** are trend plots for each of the eighty-three (83) monitoring wells. These plots show the MTBE concentration over time and also show the relative depth to water trend line, if such the data were available.

Before evaluations of this data could be conducted, it was critical to first determine the distribution of the dataset. This was done by determining how the data was statistically distributed. Many statistical tests assume a normal distribution, and violating this assumption would lessen the reliability of such statistical tests.

First, the data was tabulated in Excel ® and averages for each parameter for each monitoring well, pre- and post-ban, were calculated. This resultant data was then imported into IBM ® SPSS ® Statistics (version 20, release 20.0.0). Once in SPSS ®, the data was analyzed by running a Shapiro-Wilk test to determine if this study's data fits into a normal distribution. The Shapiro-Wilk test (Shapiro and Wilk, 1965) utilizes that null-hypothesis method to determine if a normal distribution could be used to describe the sample. If the null-hypothesis is upheld, the sample is normally distributed. Whereas, if the null-hypothesis is rejected, then the sample is not normally distributed. With an α level of 0.05, the null-hypothesis would be rejected and the sample would be determined not to be normally distributed if the probability of the outcome or p-value is less than 0.05. Conversely, if the p-value is greater than the α level, the null hypothesis cannot be rejected and the sample

may be normally distributed. Recent analysis by Razali and Wah (2011) confirms previous analysis that the Shapiro-Wilk test is the most powerful of the common formal tests for normality.

In addition to the formal normality test, visual inspection of graphical representations of the data were performed using SPSS ®. The data was shown in histograms and box plots to visually determine if the data was skewed or normally distributed about the mean. Histograms were generated in three ways: for the entire data set, for the pre-ban data, and for the post-ban data. The resultant histograms were compared to a normal distribution to determine if the data could be approximated to be normally distributed.

Next, SPSS ® was used to generate box plots in three ways: for the entire data set, pre-ban data, and post-ban data. Box plots were used to visually determine the dispersion and skewness of the data.

Another method used to analyze the data was through descriptive statistics of the data, such as determining a sample's mean, standard deviation, skewness, and kurtosis. These statistics were run using SPSS ®, and the pre-ban and post-ban data sets were evaluated. All of these tests can be used to illustrate how the data distributed, how it is skewed, how it may fit a Gaussian distribution, how it is spread about the mean, and how the mean compares to the median. Although these methods may be overlooked in favor of more robust evaluations, further evaluation

of skewness and kurtosis, for example, can help provide insight into the data that cannot be gleaned from visual evaluations alone (Doane and Seward, 2011).

If the data were found not to be normally distributed, it would require the use of non-parametric statistical tests that do not operate under the assumption of data normality (Cramer, 1998).

Site data and monitoring well-specific data were evaluated in several ways to determine how the concentration of MTBE changed in the natural environment in relation to the ban. Each of the site- or monitoring well-specific evaluation techniques are further described below.

Site-Specific Data Evaluation

Using the SPSS ® database of MTBE concentration for all sites and monitoring wells, the data was split into twenty-two (22) databases of MTBE concentration by site and sorted by date and whether the data were from before or after the ban. Using each site database, descriptive statistics were generated using SPSS ® for pre-ban and post-ban time periods for each site. In addition, histograms, box plots, and trend plots comparing the pre-ban and post-ban time periods were generated in SPSS ®.

Since the data collected for this study is from observations before and after a set time, resulting in pre-ban and post-ban time periods, it is appropriate to consider data from the two ban periods to be paired. Frank Wilcoxon (1945) proposed a

method for determining the difference in paired data sets. The test, now known as the Wilcoxon Signed-Rank Test, assumes the data come from the same population and each pair is independent. This nonparametric test, unlike the more common Paired t Test, does not assume that the data is normally distributed (Gilbert, 1987). This method could be used to determine if there is a statistically-significant difference between the two paired values by calculating the difference in the pairs, ranking the absolute differences, and then assigning corresponding signs to each rank.

The null hypothesis that the mean of pre-ban MTBE concentration at the twenty-two (22) sites is equal to its paired post-ban mean MTBE concentration is evaluated in this test.

$$H_0: \mu_1 = \mu_2 \qquad (3.1)$$

where:

$H_0 =$ the null hypothesis
$\mu_1 =$ the mean of pre-ban MTBE concentration at all sites
$\mu_2 =$ the mean of post-ban MTBE concentration at all sites

Rejecting the null hypothesis would support the alternative hypothesis that one mean is larger than the other.

SPSS ® compares two paired data sets and returns *Ranks* and *Test Statistics*. *Ranks* report the number of negative ranks, positive ranks, and ties between the two variables. Also reported is the sum of the positive and sum of the negative

ranks. The *Test Statistics* reports the Z score calculated using the lesser of the positive or negative ranks, where N is reduced by the number of ties, if any. SPSS ® calculates the exact Z score, relative to a normal distribution. In addition, the p-value (asymptotic significance for two-tailed test) is reported.

Monitoring Well-Specific Data Evaluation

The data was also evaluated for each of the eighty-three (83) monitoring wells. The graphs were visually analyzed in Excel ® (see **Appendix A**) to rule out sampling bias by using trend plots of MTBE and depth to groundwater for each monitoring well. If a monitoring well was not constructed with the appropriate screened interval, dramatic changes in MTBE concentration may appear related to changes in depth to water. This issue can occur when a portion of the formation or the plume falls outside of the screened interval due to changes in groundwater elevation. These changes are important, as groundwater analytical results are based on the average aqueous contaminant concentration for all portions of the aquifer screened by the well and weighted by the conductivity of each transmissive zone (Martin-Hayden and Robbins, 1997).

Also, using the data tables in Excel ®, the means and standard deviations were calculated from the pre-ban and post-ban MTBE data sets for each of the eighty-three (83) monitoring wells. Further analysis was conducted using SPSS ®. Similar to the process for site-specific data, the Wilcoxon Signed-Rank test was also run in SPSS ® for the pre-ban and post-ban means for each monitoring well.

The concept that became the now-named Mann-Kendall test was introduced by Henry B. Mann in 1945. Mann proposed a rank test, thereby creating a nonparametric test, to test against the data being randomly distributed and following a negative trend. He also explained that the same test could be used to disprove a randomness against a positive trend alternative hypothesis. Mann theorized though that the use of ranks may be considered by some to be "throwing away information," it was still the "most powerful test with respect to a substantial class of alternatives" (Mann, 1945).

Kendall (1975) later advanced this test by determining that the statistic proposed by Mann (1945) would approximate a normal distribution, as the tests was based on ranks. Using normal approximation, the outcomes could be reported in p-values and compared to an α level, giving the results more value. This enhanced test has come to be one of the most-commonly used tests for determining trends in hydrologic data analysis, due to its use of ranks and nonparametric nature. Its construction is well suited for hydrologic data, which is often not normally distributed, skewed, and often contains data outliers (Hamed, 2008).

The Mann-Kendall test, which is used to determine if there is a statistically significant monotonic trend (i.e., increasing or decreasing), was used to analyze MTBE concentration trend over the study period for each of the eighty-three (83) monitoring wells. This test does not require a normal distribution (i.e., nonparametric test), and as such, it is appropriate to evaluate potential trends for

any distribution (Gilbert, 1987). When comparing the t Test for trend analysis to the Mann-Kendall test, Önöz and Bayazit (2003) determined that the Mann-Kendall test was more appropriate for evaluating skewed data.

MTBE concentration data for the eighty-three (83) monitoring wells was evaluated for this analysis. Starting with the data tables of MTBE concentrations tabulated in Excel ®, the concentration data for each of the eighty-three (83) monitoring wells was imported into Minitab ®, Release 14 for further analysis. The Mann-Kendall test was constructed to determine if the data met the null hypothesis (H_0) that the data was determined to be random, at the selected alpha level of α = 0.1, or if it met one of the alternative hypotheses (Ha) and was determined to be increasing (Ha: Upperward trend) or decreasing (Ha: Downward trend). An alpha level of 0.1 was used to account for the potential variability of MTBE concentration, particularly at low concentrations, that may be the result of sampling bias. For monitoring wells that contained MTBE concentrations reported as “none detected” or “below detection limit,” a MTBE concentration equal to the detection limit (unique to the subject well) was used for the purposes of the Mann-Kendall analysis. Since this is a nonparametric rank test, it can report a false trend if the detection limits for a monitoring well vary over the study period. Detection limits identified in this study ranged from 0.5 ppb to 100 ppb, and in a limited number of cases varied for individual monitoring wells. Therefore, these monitoring wells were excluded from this analysis.

Calculated Dissipation Values for MTBE

The Mann-Kendall test evaluated trends over the duration of the study period, which include the pre-ban state. It is assumed that MTBE would be released in small quantities during this time period as the result of spills, leaks from storage and dispensing systems, including vapor releases. After the ban of its use, MTBE would be moving in and out of different phases – adsorbed/desorbed to the unsaturated sediments, dissolved in soil water or groundwater, or present in soil vapor – with no MTBE being added to the system. The resultant system, with observation of MTBE concentration over time, can then be used to evaluate the rate at which MTBE dissipates in the natural environment. This rate of attenuation or dissipation takes into account all factors that may influence concentration in the aqueous environment, including advection, biodegradation, dilution, dispersion, and volatilization (Domenico and Schwartz, 1998).

Before a dissipation rate could be determined, the kinetics of the MTBE dissipation needed to be determined. It is possible that MTBE dissipation can be approximated by zero or first order kinetics. To determine which approximation fits best, Excel ® data tables of MTBE concentration were used to plot MTBE versus time. If MTBE dissipation were to follow zero order kinetics, the slope of the dissipation curve would approximate a straight line during a period of dissipation. If the slope of the dissipation curve were to exhibit an exponential decrease during a period of dissipation, MTBE dissipation would be best approximated by first order kinetics. Through visual analysis of the graphs, it can

be determined whether dissipation of MTBE was best represented by zero order or first order decay. If dissipation is best represented by zero order decay, a linear regression of the MTBE concentration versus time data could be used to determine a zero-order decay constant. However, if the decay is best represented as a first order reaction, a linear regression of a semi-log plot of log MTBE concentration versus time can be used to determine a first-order decay constant.

If a first order reaction the appropriate representation, the half-life can be calculated by the following equations, starting with the standard rate law:

$$\frac{d[C]}{dt} = -\lambda[C] \qquad (3.2)$$

where: $[C] = \text{concentration}$

$\lambda = \text{rate constant}$

Equation 3.2 can then be integrated with the following equation:

$$\int_{[C]_o}^{[C]} \frac{d[C]}{[C]} = -\int_0^t \lambda dt \qquad (3.3)$$

where: $[C]_o = \text{original concentration}$

The result of equation 3.3 is:

$$ln\frac{[C]}{[C]_o} = -\lambda t \qquad (3.4)$$

Since the half-life is the time to reach half of the original concentration, the following can be used to determine half-life values:

$$ln\frac{\frac{1}{2}[C]_o}{[C]_o} = -\lambda t\frac{1}{2} \quad (3.5)$$

where: $t\frac{1}{2} = \text{half} - \text{life}$

Solving for half-life yields the following equation:

$$t\frac{1}{2} = \frac{ln2}{\lambda} = \frac{0.693}{\lambda} \quad (3.6)$$

Given that the rate constant (λ) in this study is the slope of the semi-log MTBE versus time plots derived from regression, equation 3.6 can be modified to account for the difference in base:

$$t\frac{1}{2} = \frac{0.693}{\lambda * 2.303} \quad (3.7)$$

Where MTBE dissipation was noted in a monitoring well after the ban, the dissipation rate for MTBE was calculated using formula 3.7. The monitoring well-specific dissipation rates were then averaged to determine an average dissipation half-life for MTBE in groundwater.

Using the calculated dissipation half-life values for individual monitoring wells, these dissipation rates were tested against later MTBE concentrations from outside of the study period. The period of this study eclipsed two years before and two years after the ban of MTBE on January 1, 2004. The calculated dissipation

half-life for each well was based on the post-ban period. The predictive value of the dissipation rates for MTBE were tested using MTBE concentration data collected after the end of the study period at the same sites and from the same monitoring wells used in the study. Seven sites were randomly selected and evaluated for further study. The site selection criteria used for this study was applied to screen these sites and monitoring wells to ensure that the same site conditions existed. Two of the sites could not be used, as active remediation commenced after the original study period ended. Monitoring wells were selected from the remaining five sites. For the sake of reliability, only those monitoring wells that exhibited MTBE concentrations over ten (10) ppb at the end of the study period were used. Then, monitoring wells that had at least three monitoring periods with MTBE results were selected, so a trend could be observed. This selection resulted in six monitoring wells from the original seven selected sites, which represented a seven percent sample of the original eighty-three (83) monitoring wells.

Post-study period MTBE concentration data from these six monitoring wells was plotted with the post-ban MTBE concentration results. The dissipation trend line that was previously calculated was added to the plot, and the post-study period data was visually evaluated compared to that monitoring well's dissipation trend line.

Chapter 4. Results

The results of the Shapiro-Wilk test for normality are shown in **Table 4-1**.

Table 4-1 Shapiro-Wilk Test of Normality - MTBE Concentration.

Ban State	Statistic	df	p-value
Pre-ban	0.195	448	0.000
Post-ban	0.313	606	0.000

The p-value from the Shapiro-Wilk test clearly does not support a normal distribution with the results for pre-ban and post-ban states both equal to 0.000. This is less than the α level of 0.05, and therefore, the null-hypothesis would be rejected and the sample would be determined not to be normally distributed.

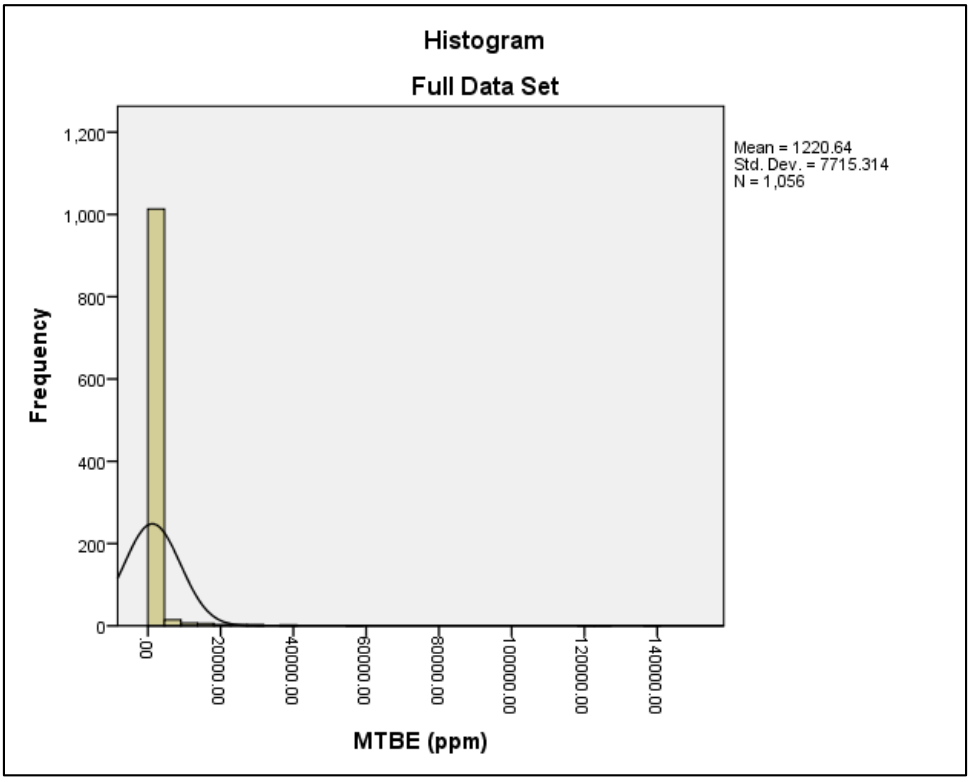
Further analysis supports this determination. An analysis of descriptive statistics, an analysis of skewness, and visual analysis of MTBE concentration trend plots for each monitoring well indicate that the data is right-skewed and approximates a lognormal distribution (see **Appendix A** and **Table 4-2**).

Table 4-2 Monitoring Well Descriptive Statistics – MTBE Concentration.

Ban State			Statistic	Std. Error
Pre-Ban	Mean		2398.37	988.91
	95% Confidence Interval for Mean	Lower Bound	431.11	
		Upper Bound	4365.63	
	5% Trimmed Mean		892.50	
	Median		135.83	
	Variance		81169343.20	
	Std. Deviation		9009.40	
	Minimum		1.33	
	Maximum		75000.00	
	Range		74998.67	
	Interquartile Range		838.58	
	Skewness		6.85	0.26
	Kurtosis		52.96	0.52
Post-Ban	Mean		347.17	88.40
	95% Confidence Interval for Mean	Lower Bound	171.32	
		Upper Bound	523.02	
	5% Trimmed Mean		198.12	
	Median		59.66	
	Variance		648564.41	
	Std. Deviation		805.33	
	Minimum		0.81	
	Maximum		3771.43	
	Range		3770.62	
	Interquartile Range		185.48	
	Skewness		3.193	0.26
	Kurtosis		9.463	0.52

The skewness analysis also fails to support the hypothesis that MTBE concentrations were normally distributed in pre-ban and post-ban states with a skewness of 6.85 (SE= 0.26) and a kurtosis of 52.96 (SE=0.52) for the pre-ban condition and a skewness of 3.19 (SE=0.26) and a kurtosis of 9.46 (SE= 0.52) for the post-ban condition.

Data histograms and box plots are shown below in **Figure 4-1** and **Figure 4-2**, respectively.



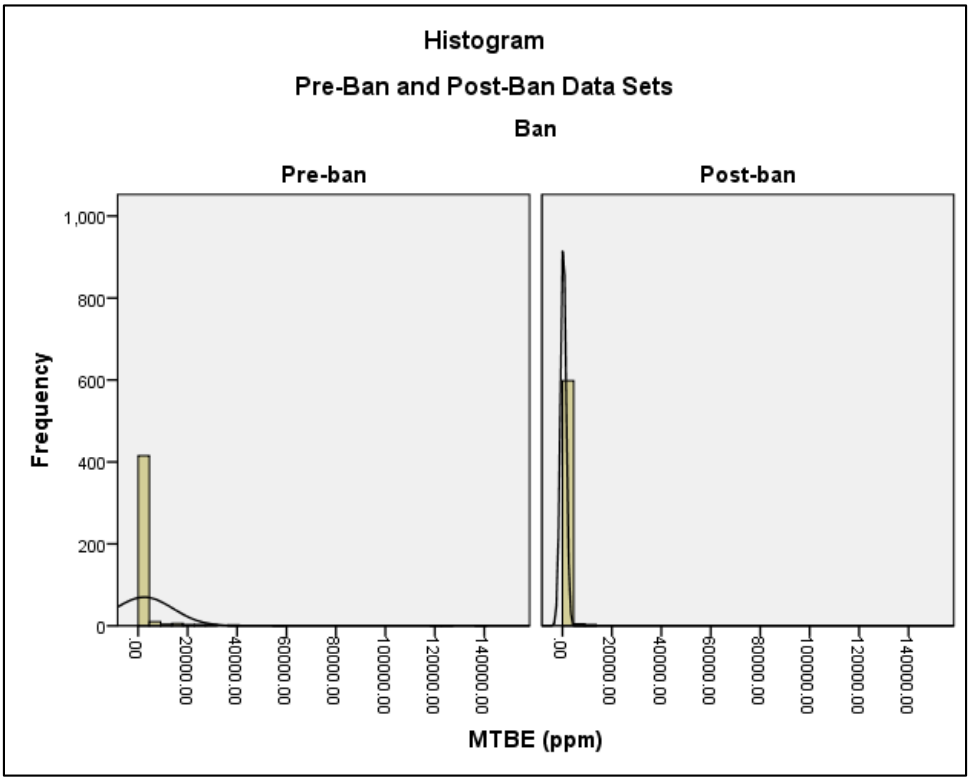


Figure 4-1 MTBE concentration histograms for the full, pre-ban, and post-ban data sets.

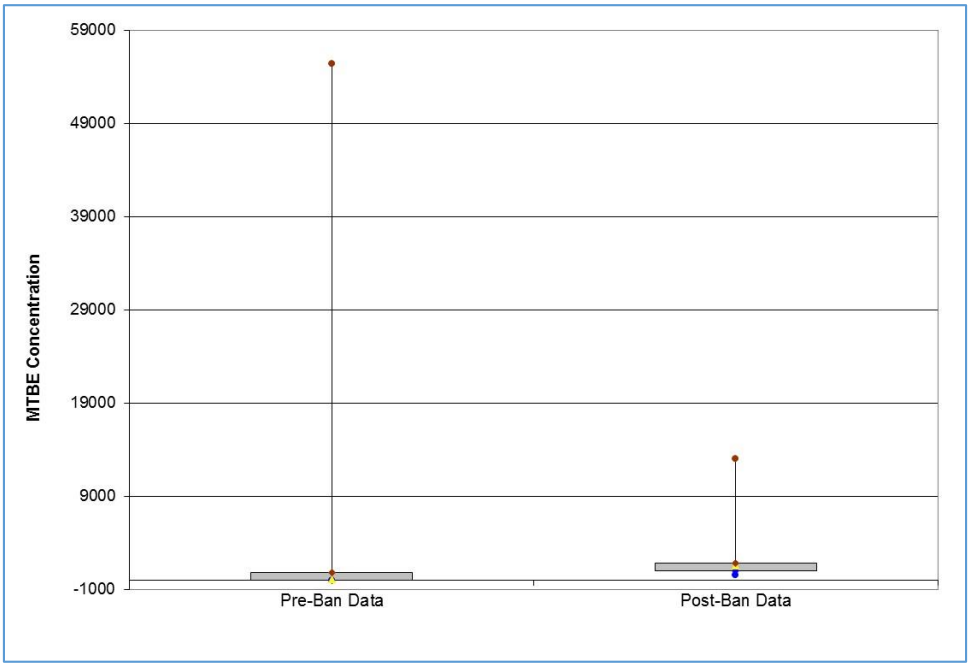


Figure 4-2 Pre-ban and post-ban box plots of MTBE concentration.

The concentration data were further evaluated on a site-by-site basis. Descriptive statistics for pooled site MTBE concentration can be found in **Appendix B** along with histograms, box plots, and MTBE concentration trend plots. **Table 4-3** provides the pre-ban and post-ban mean MTBE concentrations and standard deviations, along with the difference in means for each site.

Table 4-3 Site MTBE means, standard deviations, and difference in means.

Site	Pre-Ban Mean	Standard Deviation	Post-Ban Mean	Standard Deviation	Difference in Means
CT-01	1738	5943	717	2399	1021
CT-02	232	272	150	297	82
CT-03	7820	15698	858	1966	6962
CT-04	352	437	91	71	260
CT-05	19	21	2	4	16
CT-06	4882	9755	172	197	4710
CT-07	408	516	264	330	144
CT-08	55	41	94	105	*-39*
CT-09	227	708	8	8	220
CT-10	1735	5012	309	510	1426
CT-11	209	253	60	81	148
CT-12	10771	33218	477	1624	10294
CT-13	168	320	69	110	100
CT-14	589	765	98	122	491
CT-15	102	109	109	104	*-7*
CT-16	1494	1793	3	4	1491
CT-17	392	707	1	0	391
CT-18	918	442	159	263	759
CT-19	171	227	55	83	116
CT-20	224	390	1116	1413	*-892*
CT-21	4948	7521	992	1924	3955
CT-22	34	55	81	257	*-47*

As is seen in the table above, the MTBE concentration mean for a site's pre-ban state is greater than its post-ban state in eighteen (18) of twenty-two (22) sites, or at over eighty (80) percent of the sites. This is a simple comparison and is not reported with any level of statistical significance. The average difference in means shows a decrease in concentration between ban states of 1,436 and a standard deviation of 2,709.

The more robust Wilcoxon Signed-Rank Test also supports that the pre-ban state has greater MTBE mean concentrations than the post-ban state for pooled site

MTBE concentrations. **Table 4-4** shows that the null hypothesis is rejected and the alternative hypothesis, that the pre-ban MTBE mean concentrations are larger than the post-ban mean concentrations, is strongly supported, with a Z score of -3.360 (based on the negative ranks) at a p-value of 0.001.

Table 4-4 Wilcoxon Signed-Rank Test – Pre-Ban and Post-Ban Site MTBE Concentration.

	Ranks	N	Mean Rank	Sum of Ranks
Pre-Ban MTBE - Post-Ban MTBE	Negative Ranks	4[a]	5.75	23.00
	Positive Ranks	18[b]	12.78	230.00
	Ties	0[c]		
	Total	22		

a. Pre-Ban MTBE < Post-Ban MTBE
b. Pre-Ban MTBE > Post-Ban MTBE
c. Pre-Ban MTBE = Post-Ban MTBE

Test Statistics[a]

	Pre-Ban MTBE - Post-Ban MTBE
Z	-3.360[b]
Asymp. Sig. (2-tailed)	.001

a. Wilcoxon Signed Ranks Test
b. Based on negative ranks.

Evaluation of the data for the individual eighty-three (83) monitoring wells also showed a decrease MTBE from pre-ban to post-ban states. **Table 4-5** shows the mean MTBE concentration for each monitoring well for its pre-ban and post-ban states, as well as the difference in means.

Table 4-5 Monitoring Well MTBE Means, Standard Deviations, and Difference in Means.

Site	Site Name	Wells	Mean MTBE Pre-Ban Concentration (ppb)	Mean MTBE Post-Ban Concentration (ppb)	Difference in Means
CT-01	Ashford	MW-1	5179.9	1457.9	3722.0
		MW-2	135.8	121.0	14.8
		MW-3	5.0	143.2	*-138.2*
		MW-4	332.9	403.4	*-70.5*
CT-02	Branford-1	MW-1	128.0	79.7	48.3
		MW-2	1.3	18.0	*-16.7*
		MW-3	435.4	66.7	368.7
		MW-4	305.3	411.6	*-106.3*
CT-03	Branford-2	MW-1	3464.6	776.9	2687.7
		MW-2	10530.8	158.0	10372.8
		MW-3	25.8	1.0	24.8
		MW-4	25559.0	3342.3	22216.7
		MW-5	66.7	10.2	56.5
CT-04	Branford-3	MW-1	1029	139.9	889.1
		MW-2	69.7	15.1	54.6
		MW-3	87.3	70.9	16.4
		MW-4	220.3	139.7	80.6
CT-05	Colchester	MW-1	19.9	4.2	15.7
		MW-2	8.3	2.1	6.2
		MW-3	14.1	2.4	11.7
		MW-4	32.6	1.2	31.4
CT-06	Danbury	MW-1	411.8	294.8	117.0
		MW-2	11588.3	49.5	11538.8
CT-07	Darien	MW-1	19.1	6.8	12.3
		MW-2	996.1	459.4	536.7
		MW-3	575.1	524.1	51.0
		MW-4	13.6	67.3	*-53.7*
CT-08	East Haven	MW-1	42.7	19.0	23.7
		MW-2	54.2	248.5	*-194.3*
		MW-3	43.1	6.5	36.6
		MW-4	85.5	100.1	*-14.6*
CT-09	Essex	MW-1	48.4	7.7	40.7
		MW-2	88.0	14.1	73.9
		MW-3	545.9	1.6	544.3

CT-10	Fairfield	MW-1	57.0	44.2	12.8
		MW-2	1177.5	295.9	881.6
		MW-3	922.3	58.5	863.8
		MW-4	4782.5	889.8	3892.7
CT-11	Farmington-1	MW-1	218.6	59.7	158.9
		MW-2	197.1	61.0	136.1
CT-12	Farmington-2	MW-1	63.7	21.7	42.0
		MW-2	85.6	12.3	73.3
		MW-3	19.8	6.2	13.6
		MW-4	24.8	1.0	23.8
		MW-5	75000	3304.8	71695.2
		MW-6	1255.3	71.0	1184.3
		MW-7	732.0	3.9	728.1
CT-13	Groton-1	MW-1	124.9	35.7	89.2
		MW-2	806.5	198.3	608.2
		MW-3	67.5	43.6	23.9
		MW-4	60.5	29.7	30.8
		MW-5	72.0	30.6	41.4
CT-14	Groton-2	MW-1	262.2	198.5	63.7
		MW-2	915.7	62.7	853.0
CT-15	Guilford	MW-1	78.2	121.9	*-43.7*
		MW-2	154.3	114.3	40.0
		MW-3	74.3	26.0	48.3
CT-16	Hamden	MW-1	1895.3	3.2	1892.1
		MW-2	1092.6	3.1	1089.5
CT-17	Lisbon	MW-1	583.0	0.8	582.2
		MW-2	57.1	1.1	56.0
CT-18	New Fairfield	MW-1	726.7	26.6	700.1
		MW-2	887.0	35.8	851.2
		MW-3	1093.3	433.4	659.9
CT-19	New Haven	MW-1	150.4	75.1	75.3
		MW-2	90.0	12.4	77.6
		MW-3	200.8	110.3	90.5
		MW-4	242.5	28.1	214.4
CT-20	Rocky Hill	MW-1	612.2	2757.8	*-2145.6*
		MW-2	5.3	112.3	*-107.0*
		MW-3	9.8	271.9	*-262.1*

CT-21	Westport	MW-1	22.6	30.2	*-7.6*
		MW-2	14.6	8.0	6.6
		MW-3	42.3	22.8	19.5
		MW-4	18653.6	3771.4	14882.2
		MW-5	353.2	144.0	209.2
		MW-6	5301.6	954.3	4347.3
		MW-7	8086	1136.1	6949.9
		MW-8	9433.3	3164.0	6269.3
		MW-9	93.6	48.5	45.1
CT-22	Willington	MW-1	57.6	199.6	*-142*
		MW-2	1.7	18.7	*-17.0*
		MW-3	43.5	12.8	30.7

Sixty-eight (68) monitoring wells, or eighty-two (82) percent of the wells, exhibit a decrease in MTBE concentration when the pre-ban and the post-ban states are compared. MTBE concentration decreases on average 2,058 ppb from the pre-ban state to the post-ban state, and the differences in means have a standard deviation of 8,486.

Again, the Wilcoxon Signed-Rank test for comparison of mean pre-ban and post-ban MTBE concentration for each monitoring well supports this decrease in concentration. **Table 4-6** shows that the null hypothesis is rejected and there is strong support for the pre-ban mean being statistically greater than the post-ban mean (Z score = of -5.548, based on positive ranks, at a p-value of 0.000).

Table 4-6 Wilcoxon Signed-Rank Test for Site Pre-Ban and Post-Ban Mean MTBE Concentration.

	Ranks	N	Mean Rank	Sum of Ranks
MTBE Post-ban - MTBE Pre-ban	Negative Ranks	68[a]	43.60	2965.00
	Positive Ranks	15[b]	34.73	521.00
	Ties	0[c]		
	Total	83		

a. MTBE Post-ban < MTBE Pre-ban
b. MTBE Post-ban > MTBE Pre-ban
c. MTBE Post-ban = MTBE Pre-ban

Test Statistics[a]

	MTBE Post-ban - MTBE Pre-ban
Z	-5.548[b]
Asymp. Sig. (2-tailed)	.000

a. Wilcoxon Signed Ranks Test
b. Based on positive ranks.

The trend over the study period also show a statistically-significant decrease in MTBE concentration for a majority of the eighty-three (83) monitoring wells using the Mann-Kendall test, at the a value of 0.1.

A decreasing trend was determined to be statistically significant for fifty-one (51), or sixty-one (61) percent, of the wells in the study. No trend was determined to exist for thirty-one (31) percent of the wells. Whereas, a statistically significant increasing trend exists for six of the eighty-three (83) wells. **Table 4-7** summarizes the results of the Mann-Kendall trend analysis, and the full results are available as **Appendix C**.

Table 4-7 Summary of Mann-Kendall Trend Analysis of MTBE Concentration.

Trend Observed	Number	% of Total
DECREASE	51	61.40%
INCREASE	6	7.20%
NO TREND	26	31.30%

Appendix D shows the semi-log MTBE plots. These plots show that MTBE dissipation approximates a first order trend. These log (MTBE) versus time graphs were created using the post-ban state data tables in Excel ®, and therefore, are representative of the dissipation of MTBE after its ban. The Excel ® regression function was used to determine the best-fit trend for log (MTBE) concentration over time, and this trend line fits a first order reaction. The slope represents the rate of change in the log (MTBE) values – either positive (increasing concentrations) or negative (decreasing concentrations). The absolute magnitude of the slope indicating the magnitude of increasing or decreasing rate.

The dissipation half-life was calculated for each monitoring well that exhibited a decreasing MTBE concentration after the ban of MTBE. (It is assumed that if MTBE concentration was increasing after the ban, there had been an unreported release and this data should not be considered, as it violates the data selection criteria.) The calculated dissipation half-life (in months) for each well is presented in **Table 4-8** along with the surficial materials of the site, location of the monitoring wells (source area versus near field), and whether the monitoring wells are

screening overburden materials or completed in bedrock. As is illustrated in **Figure 4-3**, the dissipation half-life values follow a lognormal distribution.

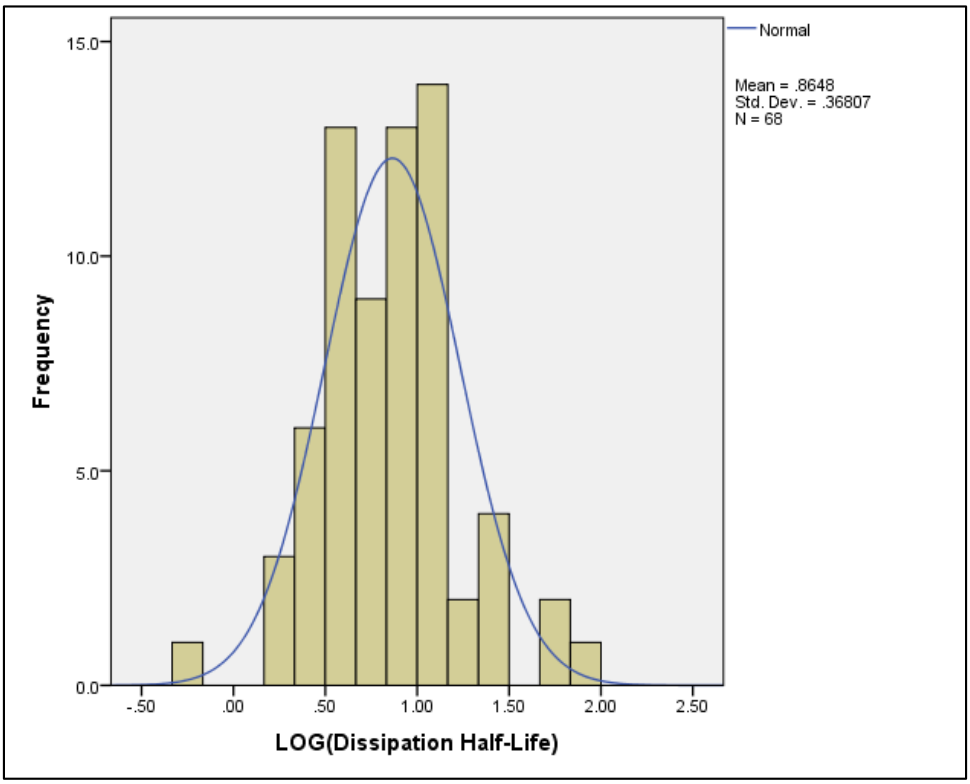


Figure 4-3 Histogram of log (dissipation half-life) values.

Table 4-8 Dissipation Rate for MTBE in Monitoring Wells with Decreasing Trend.

Site	Site Name	Surficial Materials	Wells	Source or Near Field	Screened Unit	Dissipation Half-Life of MTBE (months)
CT-01	Ashford	Sand and Gravel	MW-1	Source Area	Overburden	2.68
			MW-2	Source Area	Overburden	1.96
			MW-3	Near Field	Overburden	2.41
			MW-4	Near Field	Overburden	2.71
CT-02	Branford-1	Till, Fill or Other Deposits	MW-1	Near Field	Overburden	3.85
			MW-2	Near Field	Overburden	7.16
			MW-3	Near Field	Overburden	No Dissipation
			MW-4	Source Area	Overburden	3.02
CT-03	Branford-2	Till, Fill or Other Deposits	MW-1	Source Area	Overburden	2.11
			MW-2	Source Area	Overburden	5.91
			MW-3	Source Area	Overburden	0.64
			MW-4	Source Area	Overburden	4.04
			MW-5	Near Field	Overburden	85.97
CT-04	Branford-3	Till, Fill or Other Deposits	MW-1	Source Area	Overburden	No Dissipation
			MW-2	Near Field	Overburden	21.04
			MW-3	Near Field	Overburden	26.40
			MW-4	Near Field	Overburden	30.09
CT-05	Colchester	Sand and Gravel	MW-1	Near Field	Bedrock	No Dissipation
			MW-2	Near Field	Bedrock	47.02
			MW-3	Near Field	Bedrock	13.55
			MW-4	Near Field	Bedrock	47.02
CT-06	Danbury	Till, Fill or Other Deposits	MW-1	Near Field	Bedrock	No Dissipation
			MW-2	Near Field	Bedrock	8.70
CT-07	Darien	Till, Fill or Other Deposits	MW-1	Near Field	Overburden	No Dissipation
			MW-2	Source Area	Overburden	10.90
			MW-3	Near Field	Overburden	14.47
			MW-4	Near Field	Bedrock	No Dissipation
CT-08	East Haven	Till, Fill or Other Deposits	MW-1	Source Area	Overburden	13.14
			MW-2	Source Area	Overburden	No Dissipation
			MW-3	Source Area	Overburden	No Dissipation
			MW-4	Source Area	Overburden	No Dissipation
CT-09	Essex	Sand and Gravel	MW-1	Source Area	Overburden	12.80
			MW-2	Source Area	Overburden	9.15
			MW-3	Source Area	Overburden	12.13
CT-10	Fairfield	Till, Fill or Other Deposits	MW-1	Source Area	Overburden	No Dissipation
			MW-2	Source Area	Overburden	12.64
			MW-3	Source Area	Overburden	3.65
			MW-4	Source Area	Overburden	No Dissipation
CT-11	Farmington-1	Sand and Gravel	MW-1	Near Field	Overburden	8.41
			MW-2	Near Field	Overburden	2.03

CT-12	Farmington-2	Sand and Gravel	MW-1	Source Area	Overburden	12.38
			MW-2	Source Area	Overburden	11.80
			MW-3	Near Field	Overburden	7.15
			MW-4	Near Field	Overburden	4.41
			MW-5	Near Field	Overburden	2.62
			MW-6	Near Field	Overburden	13.43
			MW-7	Source Area	Overburden	5.97
CT-13	Groton	Sand and Gravel	MW-1	Source Area	Overburden	5.73
			MW-2	Source Area	Overburden	No Dissipation
			MW-3	Source Area	Overburden	2.59
			MW-4	Source Area	Overburden	3.38
			MW-5	Source Area	Overburden	7.32
CT-14	Groton	Till, Fill or Other Deposits	MW-1	Near Field	Overburden	3.90
			MW-2	Source Area	Overburden	4.89
CT-15	Guilford	Sand and Gravel	MW-1	Source Area	Overburden	10.10
			MW-2	Source Area	Overburden	4.09
			MW-3	Source Area	Overburden	4.18
CT-16	Hamden	Sand and Gravel	MW-1	Source Area	Overburden	6.47
			MW-2	Source Area	Overburden	6.75
CT-17	Lisbon	Sand and Gravel	MW-1	Source Area	Overburden	22.62
			MW-2	Source Area	Overburden	No Dissipation
CT-18	New Fairfield	Till, Fill or Other Deposits	MW-1	Near Field	Overburden	4.53
			MW-2	Source Area	Overburden	4.52
			MW-3	Source Area	Overburden	3.94
CT-19	New Haven	Till, Fill or Other Deposits	MW-1	Near Field	Overburden	7.00
			MW-2	Near Field	Overburden	8.29
			MW-3	Near Field	Overburden	9.96
			MW-4	Near Field	Overburden	No Dissipation
CT-20	Rocky Hill	Till, Fill or Other Deposits	MW-1	Source Area	Overburden	30.71
			MW-2	Source Area	Overburden	No Dissipation
			MW-3	Source Area	Overburden	13.43
CT-21	Westport	Till, Fill or Other Deposits	MW-1	Source Area	Overburden	5.71
			MW-2	Source Area	Bedrock	7.74
			MW-3	Near Field	Bedrock	6.46
			MW-4	Source Area	Bedrock	7.03
			MW-5	Near Field	Bedrock	16.35
			MW-6	Near Field	Bedrock	11.71
			MW-7	Near Field	Bedrock	8.57
			MW-8	Near Field	Bedrock	6.69
			MW-9	Near Field	Bedrock	4.08
CT-22	Willington	Sand and Gravel	MW-1	Source Area	Overburden	3.90
			MW-2	Source Area	Overburden	10.63
			MW-3	Source Area	Overburden	9.61

The calculated dissipation half-life for MTBE for each well has a geometric mean of approximately 7.3 months with a standard deviation of 2.3 months.

Semi-log plots of MTBE concentrations, **Figure 4-4** through **Figure 4-9**, show the predictive value of the calculated dissipation half-life values for the six monitoring wells selected to evaluate post-study period MTBE data. These semi-log plots include the MTBE concentration values from the post-ban monitoring events for each well and the monitoring results after the study period.

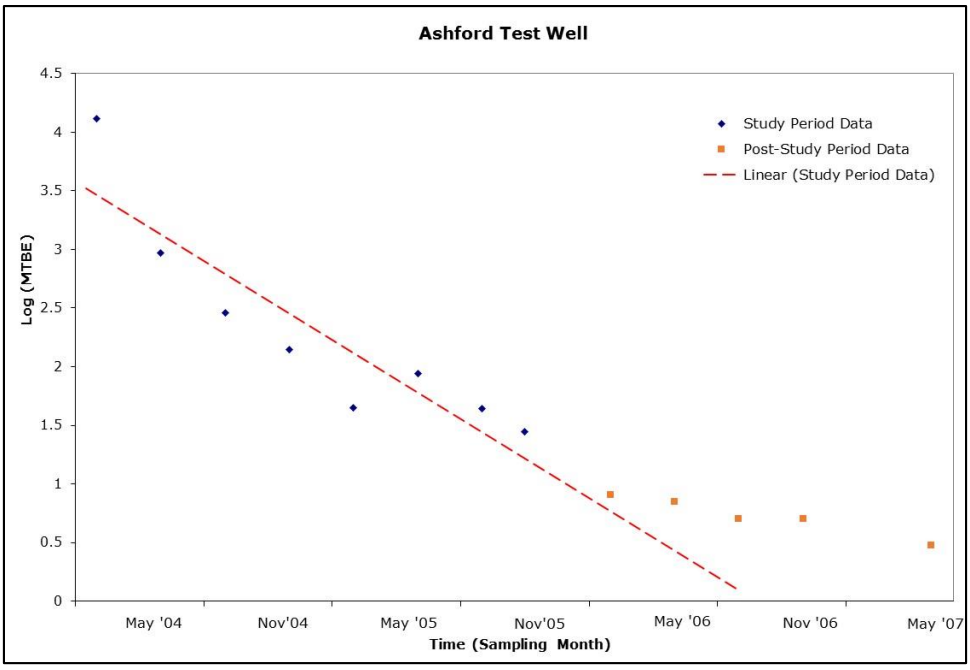


Figure 4-4 Dissipation of MTBE – Ashford test monitoring well. Log (MTBE) Concentration versus time.

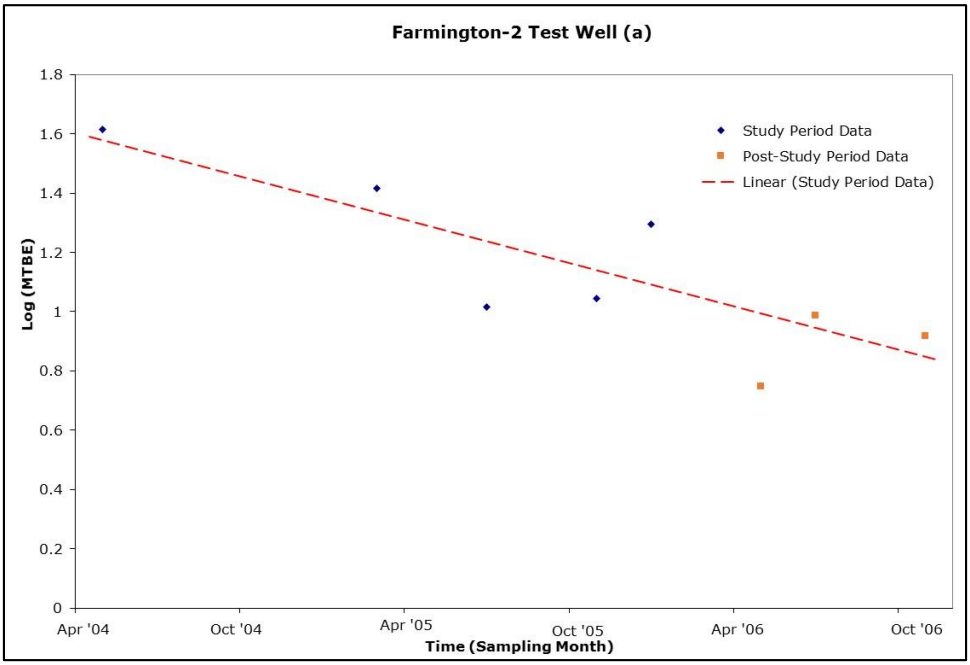


Figure 4-5 Dissipation of MTBE – Farmington-2 test monitoring well (a). Log (MTBE) Concentration versus time.

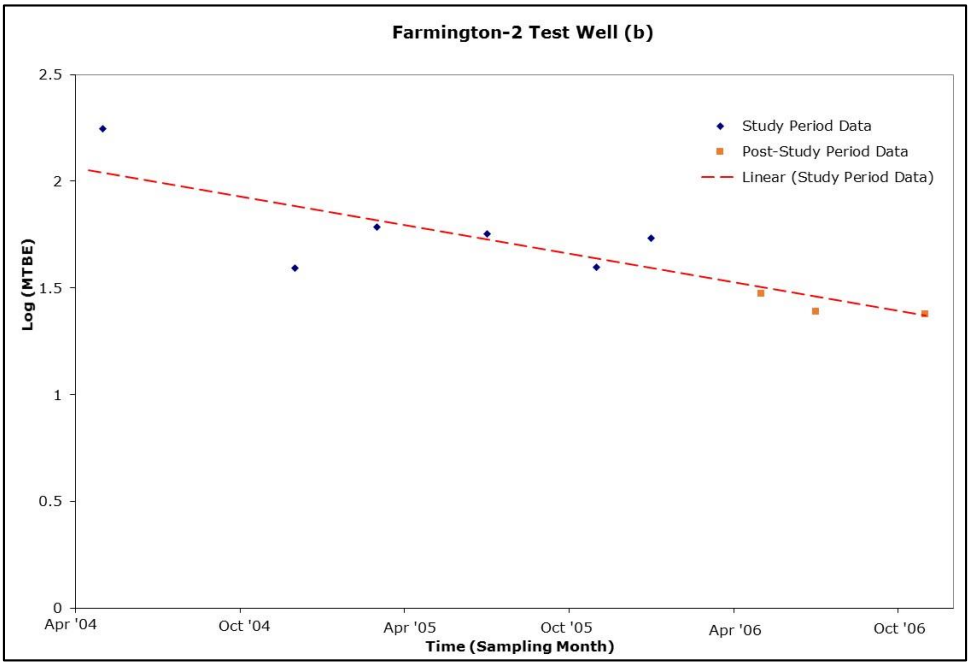


Figure 4-6 Dissipation of MTBE – Farmington-2 test monitoring well (b). Log (MTBE) Concentration versus time.

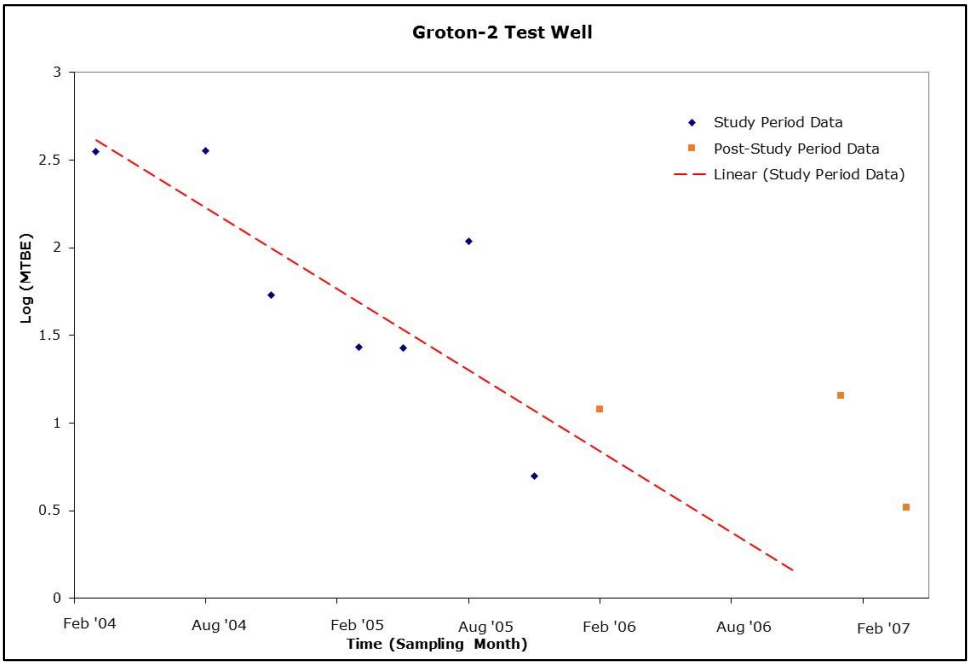


Figure 4-7 Dissipation of MTBE – Groton-2 test monitoring well. Log (MTBE) Concentration versus time.

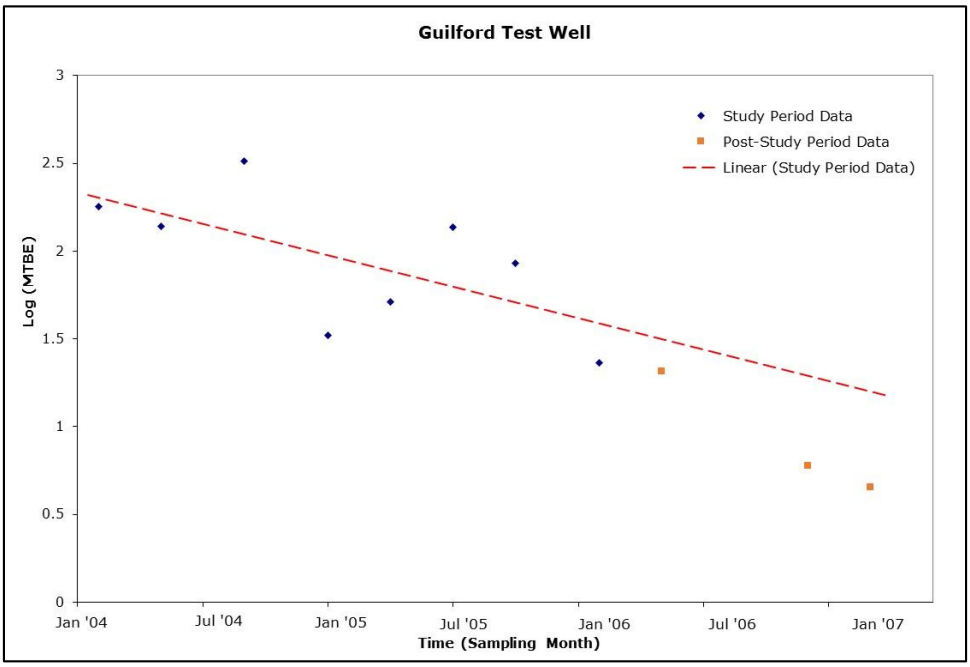


Figure 4-8 Dissipation of MTBE – Guilford test monitoring well. Log (MTBE) Concentration versus time.

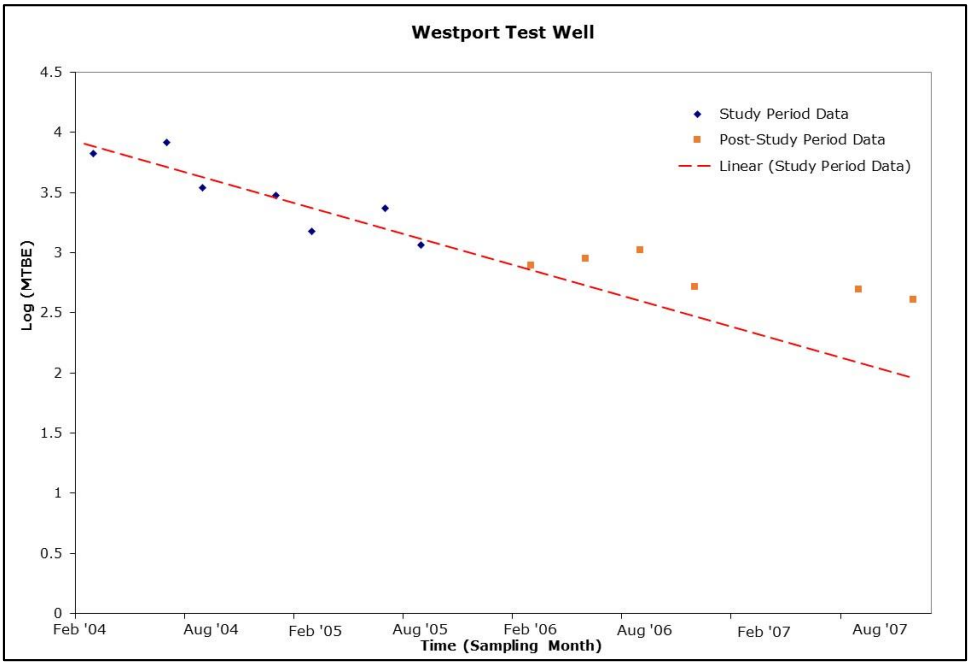


Figure 4-9 Dissipation of MTBE – Westport test monitoring well. Log (MTBE) Concentration versus time.

Chapter 5. Discussion

This study shows that MTBE dissipation in the natural environment can be modeled as a first order reaction with a half-life that ranges from approximately three weeks to just over seven years. While the spread of the data is large, sixty-six (66) percent of the dissipation values are below ten months and eighty-eight (88) percent of the values are below twenty (20) months. **Figure 5-1** illustrates the distribution of the dissipation half-life values.

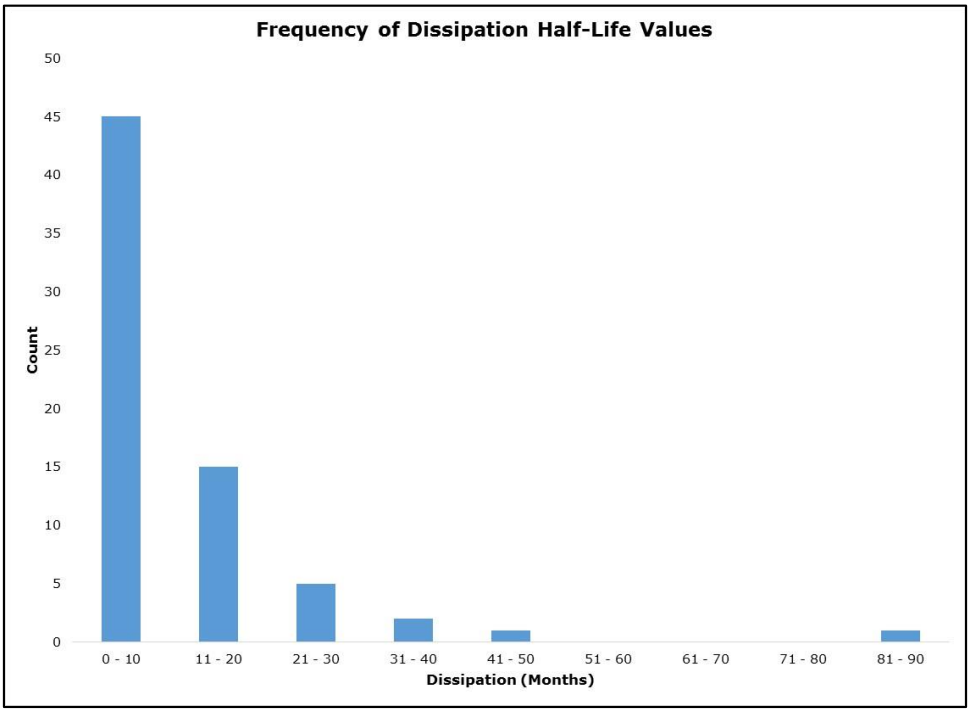


Figure 5-1 Frequency of dissipation half-life values.

Based on this skewness of half-life values, the data was further examined to determine if certain factors had a larger influence on the extreme ranges. Sites selected for this study monitored different hydrologic settings, such as sand and

gravel aquifers, various types of till, fill, and other less transmissive settings, and bedrock. In addition, this study included monitoring wells in very close proximity to the releases of MTBE and those at greater distances. **Figure 5-2** presents a box and whisker plot for different site and monitoring well characteristics to determine what factors, if any, were controlling or contributing to this variance. It can be seen that there is little difference in dissipation half-life values with respect to the characteristics examined. The most obvious characteristics that would likely have an impact on dissipation, such as transmissivity, groundwater flow velocity, and distance from a source, had little impact on the dissipation half-life results for MTBE. **Figure 5-2** illustrates that positive outliers are both common to and have an impact on the dissipation rates for each studied characteristic. The outliers all tend to represent a much longer than average dissipation, which may indicate that certain monitoring wells continued to be impacted by intermittent or on-going releases of MTBE after the date of the ban of MTBE.

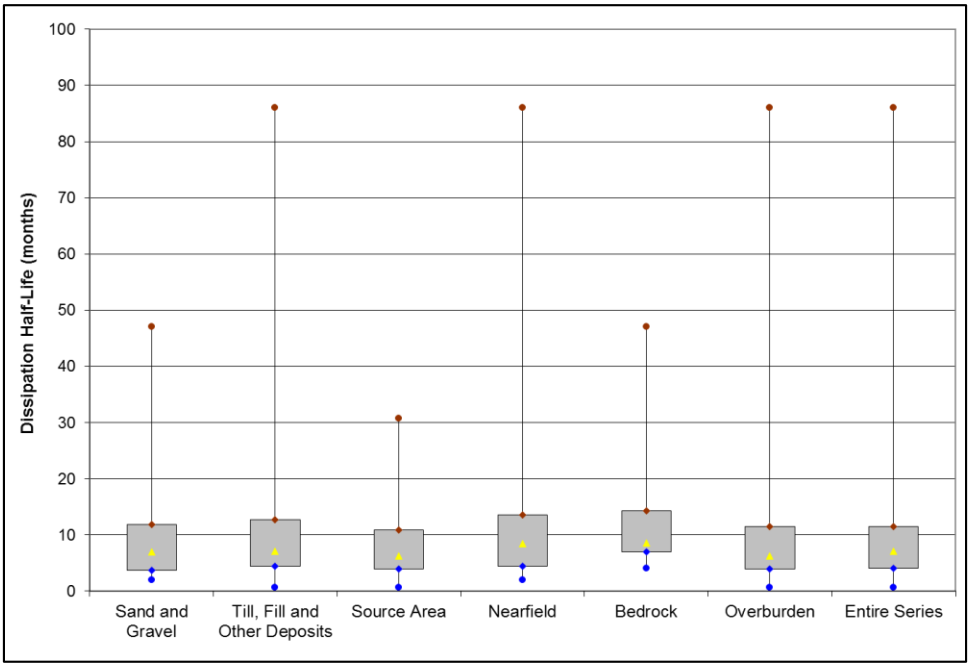


Figure 5-2 Statistical distribution of dissipation half-life values for various site and monitoring well characteristics.

Another observation of the data is that many of the monitoring wells saw a delay in dissipation of MTBE concentration beyond the January 2004 ban date. It is hypothesized that the implementation of the ban could have caused or contributed to this dissipation lag. A ban on the distribution of MTBE-containing gasoline did not stop retailers from selling their existing products that still had MTBE. Accordingly, it is unknown how long MTBE-containing gasoline was present at each site after the ban.

For illustrative purposes, **Figure 5-3, Figure 5-4,** and **Figure 5-5** show the length of time it would take for starting concentrations of MTBE ranging from ten (10) to 10,000 ppb to reach end points of 100 ppb, five ppb and one ppb, respectively. These figures were generated starting with equation 3.4, repeated below.

$$ln\frac{[C]}{[C]_o} = -\lambda t \quad (5.1)$$

If we take the concentration to be the final concentration ($[C]_f$), then time would be the time to reach the final concentration ($t[C]_f$).

$$ln\frac{[C]_f}{[C]_o} = -\lambda t[C]_f \quad (5.2)$$

where: $\lambda = 0.693/t\frac{1}{2}$

Solving for the time to reach the final concentration results in the following equation:

$$t[C]_f = -LN\frac{[C]_f}{[C]_o} / \frac{0.693}{t\frac{1}{2}} \quad (5.3)$$

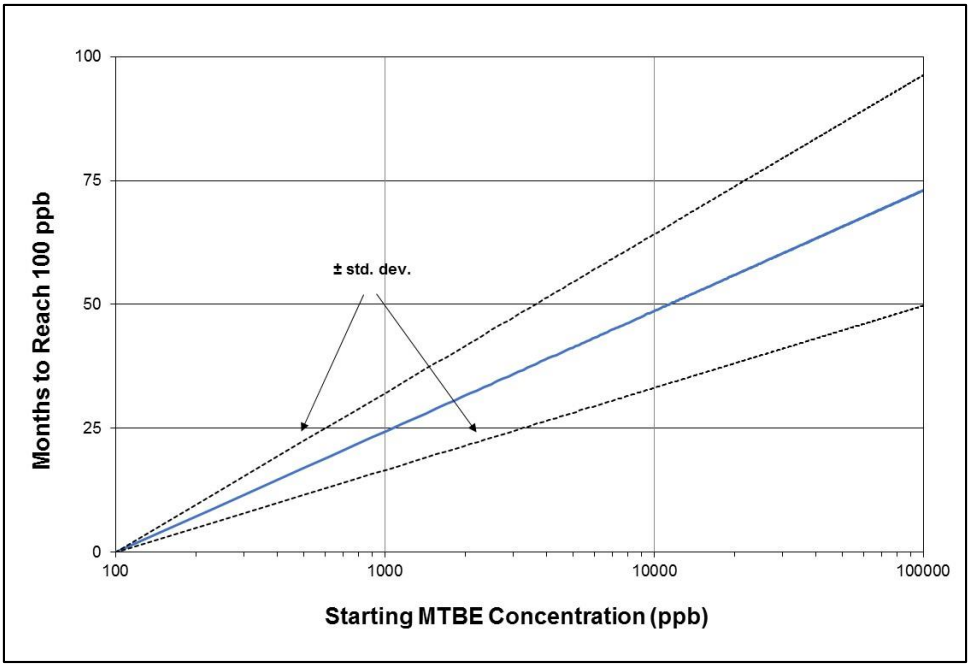


Figure 5-3. Time for a range of starting concentrations of MTBE to reach 100 ppb – based on the average calculated half-life.

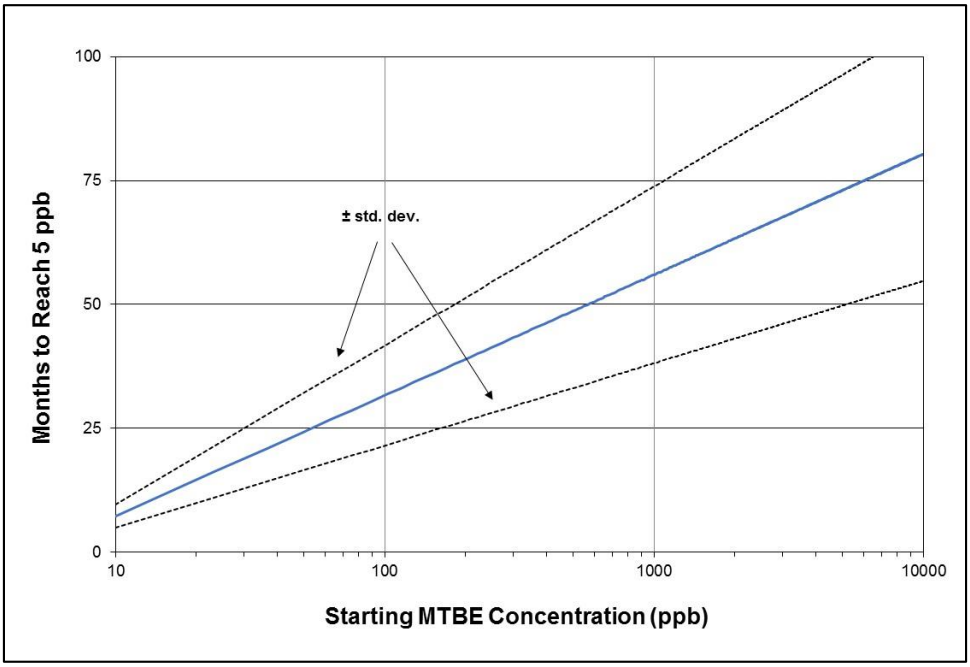


Figure 5-4. Time for a range of starting concentrations of MTBE to reach 5 ppb – based on the average calculated half-life.

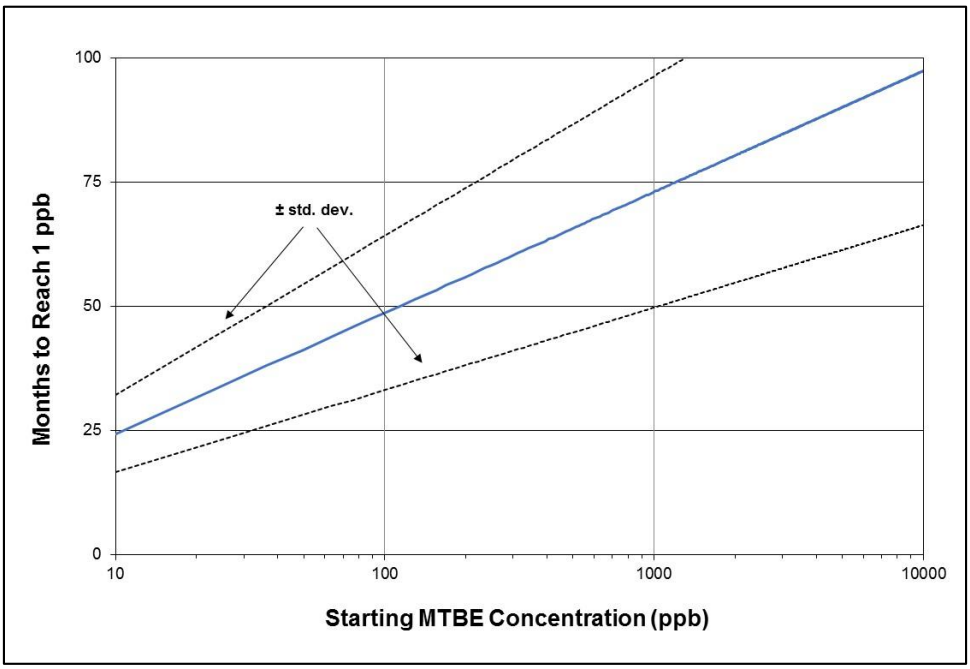


Figure 5-5. Time for a range of starting concentrations of MTBE to reach 1 ppb – based on the average calculated half-life.

As an example, it is estimated that MTBE starting at 100 ppb in groundwater would take almost two years and eight months to reach a concentration of five ppb; whereas, it would take almost four years and eight months, if the starting concentration was 1,000 ppb.

Releases of MTBE and their resultant ground water plumes can impact private and public drinking water supply wells. This study provides further information for decision-makers, as they attempt to determine how MTBE may behave in the environment. The average calculated dissipation half-life of MTBE can assist in determining how long plumes may persist at potentially problematic levels. Absent a more efficient and cost-effect ground water remedy, this study highlights the importance of quickly and completely removing the sources of pollution, especially for pollutants like MTBE that dissipate slowly. Even with thorough and prompt remedial action, MTBE present in ground water at 10,000 ppb after a complete source remediation would take eight years to dissipate to one ppb.

Chapter 6. Conclusions

The results of this study show that:

- Following a ban of MTBE, concentrations of MTBE in groundwater will decrease in a vast majority of monitoring wells at retail gasoline stations where a continuing source of MTBE is believed to be absent;
- The dissipation of MTBE, free of any on-going source, is well represented by a first order decay model;
- MTBE concentration distributions are similar from the pre-ban to the post-ban states in that they have a similar skewness (pre-ban skewness of 6.85; post-ban skewness of 3.19);
- The calculated average dissipation half-life of MTBE for this study was 7.3 months plus or minus a standard deviation of 2.3 months;
- The distribution of dissipation half-life values for MTBE is right skewed with few, high-value outliers that are likely not representative of actual natural dissipation of MTBE;
- Use of the calculated, first order dissipation rate from a period within two years from the ban was able to reasonable predict observed concentrations from periods ranging up to four years from the ban, however, the accuracy of such predictions depended on absolute concentrations; and
- Site and monitoring well characteristics that control physical, geologic, and bio-chemical parameters had little impact on the dissipation half-life values for MTBE.

REFERENCES

Clavet, C., Rubin, J., and Peckenham, J. M., 2004, Was MtBE a Costly Mistake? The Evidence from Maine: Proceedings, Northeastern Agricultural and Resource Association, 2004 Annual Meeting, Halifax, Nova Scotia.

Connecticut Department of Environmental Protection (CT DEP), 2004, Phase-Out of MTBE in Connecticut: Hartford, CT, webpage accessed August 2006.

Couch, K., Young, T., 1998, Health and Environmental Assessment of MTBE - Report to the Governor and Legislature of the State of California as Sponsored by SB 251: Volume IV, Ground & Surface Water, *Leaking Underground Storage Tanks (USTs) as Point Sources of MTBE to Groundwater and Related MTBE UST Compatibility Issues*:

Cramer, Duncan, 1998. Fundamental statistics for social research: Routledge, London.

Doane, David P. and Seward, Lori E., 2011, Measuring Skewness: Journal of Statistics Education, v. 19, no. 2, p. 1-18.

Delzer, G.C. and Ivahnenko, T., U.S. Geological Survey, 2003, Occurrence and Temporal Variability of Methyl *tert*-Butyl Ether and Other Volatile Organic Compounds in Select Sources of Drinking Water: Results of the Focused Survey, Water-Resources Investigations Report 02-4084: National Water-Quality Assessment Program, Rapid City, SD.

Domenico, Patrick A. and Schwartz, Franklin W., 1998, Physical and Chemical Hydrogeology, 2nd Edition: New York, NY: John Wiley & Sons, Inc.
Gaffney, J.S. and Marley, N.A., 2009, The Impacts of combustion emissions on air quality and climate – From coal to biofuels and beyond: Atmospheric Environment, v. 43, p. 23-36.

Energy Information Administration, 1999, Areas Participating in the Reformulated Gasoline Program: Department of Energy, Washington, DC.
Fayolle, F., Vandecasteele, J.-P. and Monot, F., 2001, Microbial degradation and fate in the environment of methyl tert-butyl ether and related fuel oxygenates: Applied Microbiology and Biotechnology, v. 56, p. 339-349.

Finneran, K.T., Lovley, D.R., 2001, Anaerobic Degradation of Methyl *tert*-Butyl Ether (MTBE) and *tert*-Butyl Alcohol (TBA): Environmental Science and Technology, v. 35 no. 9, p. 1785-1790.

Freeze, R. A. and Cherry, J., 1979, Groundwater: Englewood Cliffs, N.J.: Prentice-Hall, Inc.

Gilbert, R.O., 1987, Statistical Methods for Environmental Pollution Monitoring: New York: John Wiley & Sons, Inc.

Grady, S.J., U.S. Geological Survey, 2003, A National Survey of Methyl *tert*-Butyl Ether and Other Volatile Organic Compounds in Drinking-Water Sources: Results of the

Random Survey, Water-Resources Investigations Report 02-4079: National Water-Quality Assessment Program, East Hartford, CT.

Hamed, K., 2008, Trend detection in hydrologic data: The Mann–Kendall trend test under the scaling Hypothesis, Journal of Hydrology, v. 349, p. 350– 363

Keller, A.A., Sandall, O.C., Rinker, R.G., Mitani, M.M., Bierwagen, B. and Snodgrass, M.J, 1998b, Health and Environmental Assessment of MTBE - Report to the Governor and Legislature of the State of California as Sponsored by SB 251: Volume V, Risk Assessment, Exposure Assessment, Water Treatment & Cost-Benefit Analysis, *Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water*: University of California at Davis, Davis, CA.

Kendall, M.G., 1975, Rank Correlation Methods: London: Griffin.

Kinner, N.E., University of New Hampshire, 2001, Fate, Transport and Remediation of MTBE: Testimony before the United States Senate Committee on Environment and Public Works, Salem NH.

Leahy, M. and Holdt, B., 2006, Impact of MTBE Ban on Connecticut Public Water Systems: Proceedings, Remediation of Chlorinated and Recalcitrant Compounds, The Fifth International Conference, Monterey, CA.

Mann, H., 1945, Nonparametric Tests Against Trend: Econometrica, v. 13, no. 3, p. 245-259.

Martin-Hayden, J.M. and Robbins, G.A., 1997, Plume distortion and apparent attenuation due to concentration averaging in monitoring wells, Groundwater v. 35, no. 2, p. 339-346.

New England Interstate Water Pollution Control Commission (NEIWPCC) and Northeast States for Coordinated Air Use Management (NESCAUM), 2001, Health, Environmental and Economic Impacts of Adding Ethanol to Gasoline in the Northeast States: NEIWPCC: Lowell, MA and NESCAUM: Boston, MA.

Önöz, B. and Bayazit, M., 2003, The Power of Statistical Tests for Trend Detection, Turkish Journal of Engineering and Environmental Science, v. 27, no. 4, p. 247-251.

Razali, Nornadiah and Wah, Yap Bee, 2011: Power comparisons of Shapiro–Wilk, Kolmogorov–Smirnov, Lilliefors and Anderson–Darling tests: Journal of Statistical Modeling and Analytics, 2(1), p. 21–33.

Rice, D.W., Grose, R.D., Michaelsen, J.C., Dooher, B.P., MacQueen, D.H., Cullen, S.J., Kastenberg, W.E., Everett, L.G., and Marino, M.A., 1995, California Leaking Underground Fuel Tank (LUFT) Historical Case Analyses, UCRL-AR-122207: Environmental Protection Department, Environmental Restoration Division, Lawrence Livermore Laboratories, Livermore, CA.

Robbins, G.S., Wang, Suya., and Stuart, J.D., 1993, Using the static headspace method to determine Henry's Law constants: Analytical Chemistry, v. 65, no. 21, p. 3113-3118.

Robbins, G.A. and Gilbert, E.J. 2000, MTBE: A Conservative Tracer for Estimating Biodegradation and Hydrodynamic Dispersion at Underground Storage Tank Sites: Proceedings, International Association of Hydrogeologists, Leige, Belgium.

Shapiro, S.S. and Wilk, M.B., 1965, An Analysis of Variance Test for Normality (Complete Samples): Biometrika, v. 52 no. 3/4, p. 591-611.

Squillace, P.J., Pankow, J.F., Korte, N.E. and Zogorski, J.S., 1997, Review of the Environmental Behavior and fate of Methyl *tert*-Butyl Ether: Environmental Toxicology and Chemistry: v. 16, no. 9, p. 1836–1844.

Squillace, P.J., Pankow, J.F., Korte, N.E. and Zogorski, J.S., U.S. Geological Survey, 1998, Environmental Behavior and Fate of Methyl *tert*-Butyl Ether (MTBE): National Water Quality Assessment Program, Fact Sheet FS-203-96 (Revised 2/98).

U.S. Environmental Protection Agency, 1995, Origins of the Reformulated Gasoline Program: Office of Mobile Sources, EPA 420-F-95-001.

———1997, Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-Butyl Ether (MtBE), Office of Water, EPA 822-F-97-009.

———2007, State Actions Banning MTBE (Statewide), EPA420-B-07-013.

———2008a, FY 2008 End of Year Activity Report: Office of Underground Storage Tanks.

———2008b, Gasoline Fuels, Office of Transportation and Air Quality, webpage updated March 18, 2008.

———2008c, Regulatory Determinations Support Document for Selected Contaminants from the Second Drinking Water Contaminant Candidate List (CCL 2), Chapter 13: MTBE: Office of Groundwater and Drinking Water, EPA 815-R-08-12.

“Energy Policy Act of 2005” (PL 109-58). United States Statutes at Large, 109 (2005).

Wilcoxon, Frank, 1945, Individual Comparisons by Ranking Methods: Biometrics Bulletin, v. 1, no. 6, p. 80-83.

Yeh, Carol K. and Novak, John T., 1994, Anaerobic Biodegradation of Gasoline Oxygenates in Soils: Water Environment Research, v. 66, no. 5, p. 744-752.

Zodorski, J.S., Moran, M.J. and Hamilton, P.A., U.S. Geological Survey, 2001, MTBE and other volatile organic compounds—New findings and implications on the quality of source waters used for drinking-water supplies, Fact Sheet FS-105